Photopolymerization Shrinkage and Stress in Resins and Composites

By Jeffrey Stansbury and Junhao Ge Polymerization of conventional monomers, whether initiated thermally, photochemically or by some other means, results in a significant reduction in volume that causes difficulties in many polymer applications. The stress that arises during polymerization generates either internal or interfacial defects as well as substrate deformation. This brief review seeks to outline some of the shrinkage

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Introduction

Problems associated with polymerization shrinkage and the accompanying stress that develops as monomer converts to polymer are experienced in many photopolymerization applications. The volumetric shrinkage strain induces both internal and, via bonded surfaces, external stresses in unfilled and filled polymers intended for applications as diverse as protective coatings, microelectronic encapsulants, holographic data storage materials, microlithography, and dental adhesive/ restorative materials. The shrinkage stress is expressed through internal defect and void formation as well as substrate debonding or warpage. Residual stress can accelerate polymer deterioration and the degradation of substrate adhesion as well as enhance moisture uptake as a mechanism for stress relief.^{1,2} Features of polymerization shrinkage and shrinkage stress will be reviewed in this paper. Similarities and differences of these respective properties and their methods for measurement will be compared for unfilled thin film coatings and particulate filled, bulk polymers obtained by photopolymerization.

Polymerization Shrinkage

Addition polymerization of conventional monomers, such as methacrylates, vinyl ethers and epoxides results in volume contraction because the intermolecular separation between the monomer units is reduced to covalent bond distances in the polymer. In addition, diminished mobility of the polymer segments with respect to the separate monomers contributes to the increase in density or loss of free volume. Different monomers have different characteristic shrinkage values. The percent change in volume

FIGURE 1

Volumetric polymerization shrinkage decreases for the monomethacrylate series in the order of the methyl, ethyl, propyl, butyl, hexyl, octyl, dodecyl esters, while shrinkage on a molar basis remains relatively constant (from Patel et al.⁴).



(volumetric shrinkage) as a monomer converts to polymer is directly dependent on the reactive group concentration in the monomer and the degree of conversion in the polymer. Methacrylate monomers have been widely studied, and several investigations have shown the reduction in shrinkage that can be correlated with increasing molecular weight or molar volume of the monomer.³⁻⁵ The more informative method to evaluate shrinkage among various monomers is to compare volume change per mole of reactive group consumed (Figure 1). In this manner, the molar volume change of most methacrylates is fairly constant at 23 ± 1.8 cm³/mol C=C.⁴ The direct proportionality between conversion and shrinkage in amorphous polymeric monomethacrylates has been used as a method to determine degree of cure. In spite of the more heterogeneous nature of cross-linking polymerizations, when the incomplete conversion typically encountered in di- and multi-

methacrylate polymerizations is accounted for, the same molar shrinkage values apply.^{4, 6}

Other vinyl addition polymers, such as acrylates and vinyl ethers display similar molar volume shrinkage compared with methacrylates. For example, methyl acrylate and ethyl vinyl ether produce polymers with molar shrinkage values of 22.6 and 21.3 cm³/mol, respectively. Epoxy

EQUATION 1

A calculation used to obtain volumetric shrinkage.

shrinkage (%) = $(\underline{\rho_{p}} - \underline{\rho_{M}}) \times 100$

where $ho_{
m P}$ and $ho_{
m M}$ are polymer and monomer densities

monomers, which rely on a distinctly different ring-opening polymerization mechanism, have substantially lower shrinkage as evidenced by ethylene oxide with a molar shrinkage value of approximately 11 cm³/mol. The combination of bond breaking that Dynamic methods appropriate for real-time measurement of volumetric or 3-D photopolymerization shrinkage include dilatometry,⁸⁻¹¹ which measures specimen volume changes during polymerization via the position of a water or mercury meniscus in a

accompanies epoxide monomer addition as well as the conversion of a rigid oxirane ring to a more flexible open-chain segment in the polymer accounts for the reduced levels of shrinkage. Polymerization shrinkage in composites is reduced as filler is added and reactive monomer is displaced. The reduction in shrinkage is directly proportional to the volume fraction of the filler added.

Measurement of Shrinkage

The methods used to determine polymerization shrinkage range from simple static techniques to elaborate dynamic procedures. Static shrinkage measurement methods include monomer/polymer densities obtained by measured dimensions, gas or liquid displacement pycnometry, 7 and buoyant mass determinations (Archimedes principle). These techniques are most conveniently applied to bulk monomer and polymer specimens rather than thin coatings. A relatively minor error often encountered in the literature concerned with polymerization shrinkage involves the simple calculation used to obtain volumetric shrinkage. The change in density should be related to polymer density rather than the density of the monomer (see Equation 1).

FIGURE 2

After calibration with known volumes, the change in height of the column of water or mercury in a capillary is used to provide volumetric polymerization shrinkage results by dilatometer. Computer-controlled devices allow collection of time-resolved shrinkage data as well as real-time compensation for thermal effects.



volumetric shrinkage.¹² Linometer measurements are less sensitive to thermal effects than are dilatometerbased results, particularly with mercury dilatometers, which essentially require thermal feedback control to compensate for the large coefficient of thermal expansion associated with mercury. Among other methods used, dynamic image analysis based on laser scanning or optical monitoring^{13,14} provide direct measurement of either linear shrinkage in films or volumetric shrinkage in droplets. A deflecting disk method (Figure 3) involves measurement of the linear displacement of a bonded compliant substrate.^{15, 16} The directionality of shrinkage, which can be particularly important in non-isotropically bonded specimens or photopolymerizations of thick specimens, can be probed by the use of embedded strain gauges that provide spatially controlled linear shrinkage data.17,18

can be assumed, which allows the

linear results to be converted to

The shrinkage of thin film coatings results in the one-dimensional decrease in film thickness. This is readily followed and analyzed by laser

capillary (Figure 2). A variety of specimen geometries and sizes (down to ~ 10 mg) can be managed by dilatometry. The use of mercury in the dilatometer has the advantage of being non-interacting with monomers and polymers so no uptake occurs as is possible with water. This makes the volume results quite reliable. However, because of the opaque nature of mercury, the options for introduction of the curing light are limited and control of the irradiation intensity is complicated by the reflective surface of mercury. There are also obvious health concerns associated with the use of mercury. A linometer uses a drop of resin or composite "sandwiched" between two disks. Polymerization is initiated by irradiation through the fixed disk while the displacement of the free disk is monitored. Care must be taken that an adequate specimen

diameter to thickness ratio is maintained to assure reliable shrinkage results. By use of a greased surface on the disks, free isotropic contraction

FIGURE 3



The deflecting disk method uses a highly compliant glass substrate, which can bond to the polymerizing resin/composite, but act as a near freely shrinking surface. interferometry (Figure 4), which can be applied to either thin film or thick specimen configurations.^{19,20} The photopolymerization contraction results in a pathlength reduction, which is followed by the constructive/ destructive intensity oscillations from the interferometer. The technique is highly sensitive, if suitable vibrational isolation of the instrument is achieved, and it allows extremely rapid data collection rates. External calibration is unnecessary since the fixed wavelength of the laser provides an internal dimensional calibration. to compliance within the polymer, whereas in glassy systems, especially as modulus rapidly increases near vitrification, dramatic stresses can be developed. Stress levels can be temporarily reduced by thermal effects associated with photopolymerization. The polymerization exotherm as well as any heating effects associated with the curing light, can increase mobility in the polymerizing system. This can increase the final conversion achieved but at the same time, an additional degree of stress is introduced for a given conversion level

FIGURE 4

Interferometric measurements of shrinkage strain rely on the change in pathlength due to the shrinkage-induced displacement of the free mirror with respect to the constant pathlength of the fixed mirror.



Polymerization Stress

As photopolymerization proceeds, modulus and other polymer properties evolve in varying relationships with conversion. Several studies have focused on this evolution of structure and properties.²¹⁻²⁶ Stress development during polymerization is a function of the instantaneous modulus and the shrinkage strain. Thus, rubbery polymers generate minimal stress due as the cured polymer returns to ambient temperature. In typical composites with high modulus fillers, effective coupling between resin and filler is required to achieve mechanical reinforcement. Compared with the filler, the higher coefficient of thermal expansion of the polymer, combined with the shrinkage isolated in the resin phase, leads to tensile stresses in the polymer matrix around the filler particles.^{27, 28}

Measurement of Polymerization Stress

Just as with shrinkage determinations, several diverse techniques have been developed to measure stress during polymerization. In the bonded disk technique, a relatively thick layer of resin or composite is photocured between two parallel surfaces, one of which is attached to a load cell that monitors the force necessary to restrict the development of shrinkage.²⁹⁻³¹ A surface treatment is necessary to assure good bonding between the substrates and the polymer. The specimen diameter to thickness ratio can be altered with the result that thinner specimens produce significantly greater stresses due to their higher proportion of bonded to non-bonded surface configuration. As expected, the measured stress that evolves during the polymerization is inversely proportional to the compliance of the test system.^{32, 33} Photoelastic analysis using polarized microscopy can provide normal and shear stresses in complex bonded geometries involving surfaces of resins and composites.34

Beam bending is commonly used to determine polymerization-induced stress development in coatings. In this approach, a known thickness of resin (typically unfilled) is photocured on a thicker, stiffer substrate of known elastic modulus and Poisson's ratio with the in-plane stress causing a radius of curvature.³⁵ The beam dimensions and material is selected to allow 2-D bending, rather than 3-D cupping, and to limit the magnitude of bending such that excessive stress relaxation through deformation is avoided. The active beam deflection can be monitored by scanning laser techniques, profilometery or interferometry. Instead of free beam deflection, a clamped cantilever with calibrated beam constants can also be used to monitor the stress generated during coating photopolymerization

FIGURE 5

The coating applied to the cantilever beam undergoes free shrinkage toward the bonded surface during photopolymerization, but the restricted in-plane shrinkage produces linear bending of the beam, from which stress can be measured.



(Figure 5). When polymerized, the inplane stresses induce substrate curl, which can be monitored by laser deflection. Displacement of the beam and the clamped beam length allow the radius of curvature to be approximated and thus, the dynamic stresses can be calculated.³⁶⁻³⁹ Of particular interest in this deflecting cantilever beam approach is the direct coupling (on same specimen) of spectroscopic data or the indirect use (from separate specimens) of calorimetric methods to determine the coating conversion profile simultaneously with the stress evolution data.^{40,41} These combined analytical techniques allow stress to be plotted dynamically against conversion. The results demonstrate that stress builds slowly as conversion rises beyond the gel point but increases rapidly as vitrification is reached.⁴² The cantilever

FIGURE 6

Filled or unfilled resin placed in a retaining sleeve is photocured along a quartz rod used as one of the fixed substrates. Silane surface treatment on the rod ends promotes polymer adhesion for effective transfer of stress to yield displacement of the cantilever beam.



beam technique has also been modified to evaluate stress development in a bonded configuration of thick resins and composites (Figure 6).⁴³

Modification of Materials to Reduce Shrinkage and/or Stress

Prior to polymerization, microscopic porosity in the resin or composite results in reduced shrinkage and stress development due to the formation of significantly enlarged voids in the polymer.44,45 The introduction of nonbonded micro-filler or nano-filler has been used to controllably achieve controlled pore structure and reduced shrinkage in composites.^{31, 46, 47} The use of a reactive filler designed to release volatile components during polymerization has also been evaluated as a means of minimizing shrinkage.48 Polymerization induced phase separation, either through selection of comonomer composition or by the use of specialized additives, can result in appreciably lower shrinkage and stress than similar systems that remain homogeneous.49-52 The addition of plasticizers or comonomers that contribute toward lower modulus coatings and bulk polymers can also significantly reduce the final stress level of the cured material. Little work has been done to determine the influence of filler on stress conveyed by bonded composites. Preliminary studies in this area point to an increase in stress as a function of filler content.⁵³ Therefore, even though filler reduces polymerization shrinkage, the corresponding increase in modulus that the filler imparts to the resin during polymerization appears to be the controlling factor in stress evolution.

Beyond the previously mentioned effects of filler to minimize shrinkage and/or stress in composite materials, there are many approaches involving monomer design that are directed toward this same goal. As mentioned, decreased reactive group concentration leads directly to reduced shrinkage for a given conversion. Thus, bulky monomers and prepolymers have been evaluated as routes to lower shrinkage and potentially, lower stress polymers.⁵⁴⁻⁵⁷ Ordered liquid crystalline monomers that ideally yield amorphous polymers is another approach to produce minimal shrinkage.58,59 Within conventional monomer compositions, increased monomer functionality, which results in increased reactive group density, provides higher levels of stress development, even at lower values of final conversion.⁴⁰ Related work establishes that cross-linking photopolymerization of methacrylate monomers reaches much higher stress levels for a given conversion compared with acrylate monomers of similar structures.42 Epoxy-based resin systems have demonstrated significantly lower stress compared with acrylate resins of similar cross-link density.²²

The University of Colorado Department of Chemical and Biological Engineering lab is currently engaged in a variety of materials approaches to achieve low shrinkage/low stress photocurable resins and composites while also developing a near-infraredbased analytical technique⁶⁰ for simultaneous monitoring of conversion and stress evolution under a wide range of photocuring protocols. These results will be the topic of a future report.

Acknowledgments

The authors acknowledge the support of the National Institutes of Health (Y1-DE1021 and R01-DE14227) for studies of photopolymerization shrinkage and stress in dental polymers.

References

 Feilzer AJ, Degee AJ, Davidson CL, "Relaxation of polymerization contraction shear stress by hygroscopic expansion." *Journal of Dental Research*, 1990;69:36-39.

- Oshida Y, Gorthy J, "Water-sorption kinetics of dental polymeric resin under tensile stressing conditions," *Bio-Medical Materials and Engineering*, 1999; 9(2):125-133.
- Loshaek S, Fox TG, Cross-linked Polymer I, "Factors influencing the efficiency in cross-linking in copolymers of methyl methacrylate and glycol dimethacrylates," *Journal of the American Chemical Society*, 1953; 75:3,544-3,550.
- Patel MP, Braden M, Davy KWM, "Polymerization shrinkage of methacrylate esters," Biomaterials, 1987; 8:53-56.
- Brandrup J, Immergut EH, Grulke EA, editors, Polymer Handbook. 4th ed. New York: John Wiley and Sons; 1999.
- Rueggeberg F, Tamareselvy K, "Resin cure determination by polymerization shrinkage," *Dental Materials*, 1995; 11(4):265-268.
- Cook WD, Forrest M, Goodwin AA, "A simple method for the measurement of polymerization shrinkage in dental composites," *Dental Materials*, 1999; 15(6):447-449.
- Oberholzer TG, Grobler SR, Pameijer CH, Rossouw RJ, "A modified dilatometer for determining volumetric polymerization shrinkage of dental materials," *Measurement Science & Technology 2002*, 13(1):78-83.
- Penn RW, "A recording dilatometer for measuring polymerization shrinkage," *Dental Materials*, 1986; 2:78-79.
- Lai JH, Johnson AE, "Measuring polymerization shrinkage of photoactivated restorative materials by water-filled dilatometer." *Dental Materials*, 1993; 9:139-143.
- Bandyopadhyay S, "A study of the volumetric setting shrinkage of some dental materials," *Journal of Biomedical Materials Research*, 1982; 16:135-144.
- Degee AJ, Feilzer AJ, Davidson CL, "True linear polymerization shrinkage of unfilled resins and composites determined with a linometer," *Dental Materials*, 1993; 9:11-14.
- Fano V, Ortalli I, Pizzi S, Bonanini M, "Polymerization shrinkage of microfilled composites determined by laser beam scanning," *Biomaterials*, 1997; 18:467-470.
- Hudson AJ, Martin SC, Hubert M, Spelt JK, "Optical measurements of shrinkage in UV-cured adhesives," *Journal of Electronic Packaging*, 2002; 124(4):352-354.
- Watts DC, Cash AJ, "Kinetic measurements of photo-polymerization contraction in resins and composites,"

Measurement Science and Technology, 1991; 2:788-794.

- Watts DC, Marouf AS, "Optimal specimen geometry in bonded-disk shrinkage-strain measurements on light-cured biomaterials," *Dental Materials*, 2000; 16:447-451.
- Sakaguchi RL, Sasik CT, Bunczak MA, Douglas WH, "Strain gauge method for measuring polymerization contraction of composite restoratives," *Journal of Dentistry*, 1991; 19:312-316.
- Sakaguchi RL, Versluis A, Douglas WH, "Analysis of strain gage method for measurement of post-gel shrinkage in resin composites," *Dental Materials*, 1997; 13(4):233-239.
- Dudi O, Grubbs WT, "Laser interferometric technique for measuring polymer cure kinetics," *Journal of Applied Polymer Science*, 1999; 74(9):2133-2142.
- Fogleman EA, Kelly MT, Grubbs WT, "Laser interferometric method for measuring linear polymerization shrinkage in light cured dental restorations," *Dental Materials*, 2002; 18:324-330.
- Dauvillier BS, Feilzer AJ, De Gee AJ, Davidson CL, "Visco-elastic parameters of dental restorative materials during setting," *Journal of Dental Research*, 2000; 79:818-823.
- Lange J, Manson J-AE, "Build-up of structure and viscoelastic properties in epoxy and acrylate resins cured below their ultimate glass transition temperature," *Polymer*, 1996; 37:5,859-5,868.
- Lange J, Toll S, Manson JAE, "Residual stress build-up in thermoset films cured below their ultimate glass transition temperature," *Polymer*, 1997; 38:809-815.
- Lange J, "Viscoelastic properties and transitions during thermal and UV cure of a methacrylate resin," *Polymer Engineering and Science*, 1999; 39:1,651-1,660.
- Sakaguchi RL, Shah NC, Lim BS, Ferracane JL, Borgersen SE, "Dynamic mechanical analysis of storage modulus development in light-activated polymer matrix composites," *Dental Materials*, 2002; 18:197-202.
- Eom Y, Boogh L, Michaud V, Sunderland P, Manson JA, "Time-curetemperature superposition for the prediction of instantaneous viscoelastic properties during cure," *Polymer Engineering and Science*, 2000; 40(6):1,281-1,292.
- 27. Darvell BW, Materials science for dentistry, 7 ed. Pokfulam: Darvell; 2002.

- Voros G, Pukanszky B, "Stress distribution in particulate filled composites and its effect on micromechanical deformation," *Journal of Materials Science*, 1995; 30:4,171-4,178.
- Feilzer AJ, Degee AJ, Davidson CL, "Setting stress in composite resin in relation to configuration of the restoration," *Journal of Dental Research*, 1987; 66:1,636-1,639.
- Alster D, Feilzer AJ, Degee AJ, Davidson CL, "Polymerization contraction stress in thin resin composite layers as a function of layer thickness," *Dental Materials*, 1997; 13(3):146-150.
- Condon JR, Ferracane JL, "Assessing the effect of composite formulation on polymerization stress," *Journal of the American Dental Association*, 2000; 131:497-503.
- Alster D, Venhoven BAM, Feilzer AJ, Davidson CL, "Influence of compliance of the substrate materials on polymerization contraction stress in thin resin composite layers," *Biomaterials*, 1997; 18(4):337-341.
- 33. Laughlin GA, Williams JL, Eick JD, "The influence of system compliance and sample geometry on composite polymerization shrinkage stress," *Journal of Biomedical Materials Research*, 2002; 63(5):671-678.
- Kinomoto Y, Torii M, "Photoelastic analysis of polymerization contraction stresses in resin composite restorations," *Journal of Dentistry*, 1998; 26:165-171.
- 35. Benabdi M, Roche AA, "Mechanical properties of thin and thick coatings applied to various substrates. An elastic analysis of residual stresses within coating materials," *Journal of Adhesion Science and Technology*, 1997; 11:281-299.
- Payne JA, McCormick AV, Francis LF, "In situ stress measurement apparatus for liquid applied coatings," *Review of Scientific Instruments*, 1997; 68(12):4.564-4.568.
- Stolov AA, Xie T, Penelle J, Hsu SL, "Stress buildup in ultraviolet-cured coatings: Sample thickness dependence," *Macromolecules*, 2001; 34(9):2,865-2,869.
- Stolov AA, Xie T, Penelle J, Hsu SL, Stidham HD, "An analysis of photopolymerization kinetics and stress development in multifunctional acrylate coatings," *Polymer Engineering and Science*, 2001; 41(2):314-328.
- 39. Francis LF, McCormick AV, Vaessen DM, Payne JA, "Development and

measurement of stress in polymer coatings," *Journal of Materials Science*, 2002; 37:4,897-4,911.

- Payne JA, Francis LF, McCormick AV, "The effects of processing variables on stress development in ultraviolet-cured coatings," *Journal of Applied Polymer Science*, 1997; 66(7):1,267-1,277.
- 41. Stolov AA, Xie T, Penelle J, Hsu SL, "Simultaneous measurement of polymerization kinetics and stress development in radiation-cured coatings: A new experimental approach and relationship between degree of conversion and stress," *Macromolecules*, 2000; 33:6,970-6,976.
- 42. Wen M, Scriven LE, McCormick AV, "Differential scanning calorimetry and cantilever deflection studies of polymerization kinetics and stress in ultraviolet curing of multifunctional (meth)acrylate coatings," *Macromolecules*, 2002; 35(1):112-120.
- Watts DC, Marouf AS, Al-Hindi AM, "Photopolymerization shrinkage-stress kinetics in resin-composites: methods development," *Dental Materials*, 2003; 19:1-11.
- 44. Alster D, Feilzer AJ, Degee AJ, Mol A, Davidson CL, "The dependence of shrinkage stress reduction on porosity concentration in thin resin layers." *Journal of Dental Research*, 1992; 71:1,619-1,622.
- 45. Eom Y, Boogh L, Michaud V, Sunderland P, Manson JA, "Stressinitiated void formation during cure of a three-dimensionally constrained thermoset resin," *Polymer Engineering* and Science, 2001; 41(3):492-503.
- Condon JR, Ferracane JL, "Reduction of composite contraction stress through non-bonded microfiller particles," *Dental Materials*, 1998; 14(4):256-260.
- Condon JR, Ferracane JL, "Reduced polymerization stress through nonbonded nanofiller particles," *Biomaterials*, 2002; 23:3,807-3,815.
- Liu C-F, Collard SM, Armeniades CD, "Constant-volume polymerization of composites by addition of ammoniamodified montmorillonite," *American Journal of Dentistry*, 1990; 3:44-50.
- 49. Kinkelaar M, Wang B, Lee LJ, "Shrinkage behavior of low-profile unsaturated polyester resins," *Polymer*, 1994;35:3,011-3,022.
- Piggott MR, Zhou WV, "Shrinkage control in fibre reinforced polymers 3. Carbon fibre reinforced polyesters with expanding monomers and low profile additives," *Polymers & Polymer Composites*, 1995; 3:395-402.

- Huang Y-J, Liang C-M, "Volume shrinkage characteristics in the cure of low-shrink unsaturated polyester resins," *Polymer*, 1996; 37:401-412.
- Vaessen DM, McCormick AV, Francis LF, "Effects of phase separation on stress development in polymeric coatings," *Polymer*, 2002; 43(8):2,267-2,277.
- Aarnts MP, Akinmade A, Feilzer AJ, "Effect of filler load on contraction stress and volumetric shrinkage," *Journal of Dental Research*, 1999; 78:482 (Abstract. No. 3014).
- Pezron E, Magny B, "Modeling of UV oligomers and monomers properties: viscosity and shrinkage," *European Coatings Journal*, 1996: 602-604.
- Choi KM, Stansbury JW, "New families of photocurable oligomeric fluoromonomers for use in dental composites," *Chemistry of Materials*, 1996; 8:2704-2707.
- 56. Klee JE, Neidhart F, Flammersheim HJ, Mulhaupt R, "Monomers for low shrinking composites, 2-Synthesis of branched methacrylates and their application in dental composites," *Macromolecular Chemistry and Physics* 1999; 200(3):517-523.
- 57. Gao F, Schricker SR, Tong YH, Culbertson BM, "Novel trimethacrylates: Synthesis, characterization, and evaluation of new monomers for improved dental restoratives," *Journal of Macromolecular Science— Pure and Applied Chemistry* 2002; 39(4):251-265.
- Holter D, Frey H, Mulhaupt R, "Branched bismethacrylates based on bis-GMA—a systematic route to low shrinkage composites," *Polymer Preprints*, 1997; 38(2).
- Rawls HR, Wellinghoff VT, Norling BK, "Low shrinkage resins from liquid crystal diacrylate monomers," ACS Polymer Preprints, 1997; 38:167-168.
- Stansbury J, Dickens S, "Determination of double bond conversion in dental resins by near infrared spectroscopy," *Dent. Mater.* 2001; 17(1):71-79.

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