

Measurement and Management of Stress Development in Photopolymer Networks

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The formation of glassy, high-modulus polymer networks with conventional crosslinking monomers is accompanied by significant volumetric shrinkage that, in turn, leads to the development of internal and external stresses. The analysis of conversion-dependent stress evolution, including real-time measurement of several critical factors associated with stress development, will be detailed in this article along with some examples of novel polymeric materials that

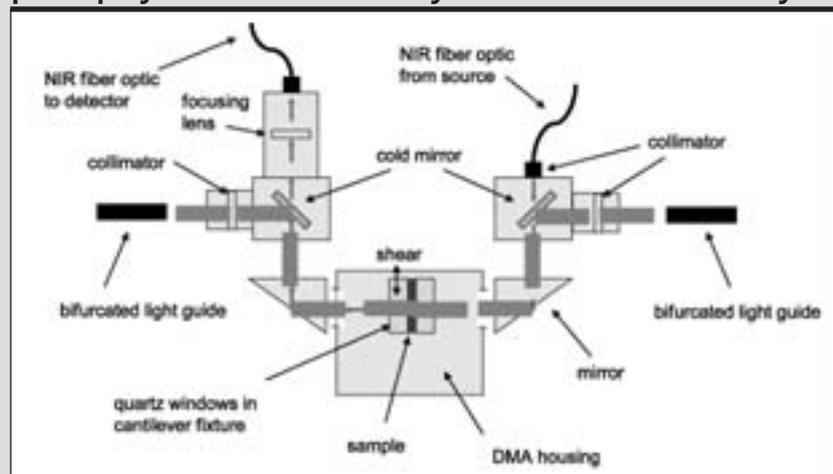
provide either chemical or physical mechanisms for stress reduction.

Many practical difficulties are encountered due to polymerization shrinkage and the accompanying stress that develops as di- and multi-vinyl monomers are converted to high-modulus polymeric networks. 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.^{1,2} Therefore, the development of analytical measurement techniques that promote the rational study of polymerization stress, and the respective factors that lead to stress development,

FIGURE 1

Optics schematic for NIR and curing light access for the measurement of shear modulus development during photopolymerization in the dynamic mechanical analyzer



is important in the overall goal of designing new procedures and materials that are capable of minimizing polymerization stress.

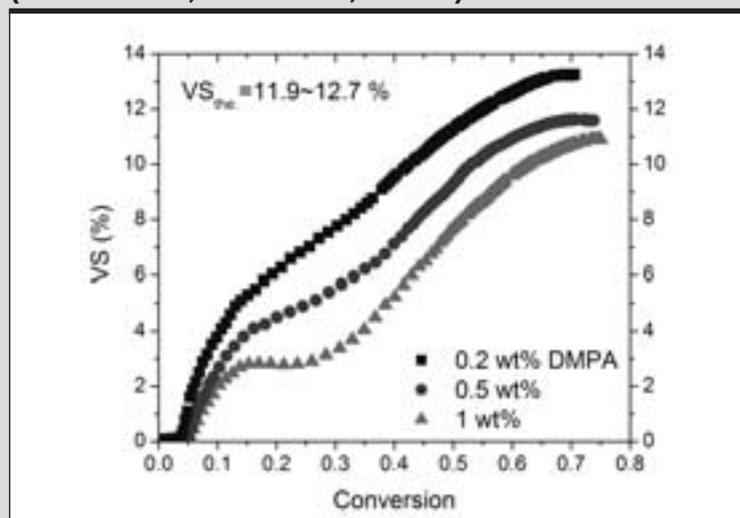
Polymerization stress in crosslinking systems is related to the product of post-gelation shrinkage strain and the material modulus. The evolution of these properties during a photopolymerization is also affected by temperature, which means that reaction kinetics and processing conditions may also contribute to overall stress development. The static final shrinkage value obtained for a polymerization can be predicted based on the initial reactive group concentration the degree of conversion attained and the molar shrinkage coefficient associated with the particular type of monomer used. Methacrylate monomers have been widely studied with a relatively consistent molar volume change of $23.6 \pm 1.8 \text{ cm}^3$ per mole of double bond reacted.³ Therefore, this contribution is focused on the dynamic measurement of shrinkage, modulus and stress during photopolymerization, along with coupled real-time conversion monitoring. An example of a materials-based approach to provide a practical, low-stress crosslinked polymer will also be used to highlight the analytical methods.

Experimental

Conversion in methacrylate polymers can be conveniently assessed using near-infrared (NIR) spectroscopy ($=\text{CH}_2$ absorbance at 6165 cm^{-1})⁴. This is compatible with a wide range of specimen configurations as well as remote signal transmission via fiber optics used here to provide real-time conversion while simultaneously monitoring the evolution of other polymer properties (such as shrinkage, modulus and stress) that are clearly conversion dependent. There are many ways to measure polymerization

FIGURE 2

Volumetric shrinkage of triethylene glycol dimethacrylate photopolymer with respect to conversion during continuous UV irradiation (320-390 nm; 4 mW/cm²; 15 min)



shrinkage. We have focused on dynamic measurement techniques and, in particular, a method that allows the coordinated measurement of conversion. A linometer (Academic Center for Dentistry Amsterdam, Department of Dental Materials Science, Amsterdam) 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. This produces dynamic linear shrinkage data that can be converted to volumetric shrinkage results and then replotted as a function of conversion.

The analysis of modulus development during polymerization is typically limited to shear or torsional measurement methods since the test procedure must accommodate the transition from the liquid monomeric state to the glassy final polymer. We have used a photo-rheometer (TA ARES) and a photo-accessible dynamic mechanical

analyzer (photo-DMA) (modified Perkin Elmer 8000; Figure 1). Both these devices have been combined with fiber-optic transmission NIR to allow the simultaneous acquisition of conversion data to index with the dynamic shear modulus results. The evolution of stress during the UV or visible light-initiated polymerization of methacrylate resins and composites is accomplished with a cantilever beam tensometer (American Dental Association PRC). This device readily permits NIR access which, in addition to final stress versus conversion results, also provides important information such as conversion at the onset of stress development (related to gel point) and the stage of the reaction representing the transition between the rubbery and the glassy states.

In demonstration of how materials can offer different mechanisms for polymerization stress reduction, a conventional dimethacrylate monomer, BisEMA (ethoxylated bisphenol A

dimethacrylate; Esstech), was photopolymerized (initiator: 2,2-dimethoxy-2-phenylacetophenone; DMPA, 0.1 wt%) in the presence of a variety of thiol chain transfer agents using UV light (60 s exposure; 500 mW/cm²; 320-390 nm). The thiols used included methyl mercaptopropionate (MMP); benzyl mercaptan (BM); benzene thiol (BT); 1,6-hexanedithiol (HDT); pentaerythritol tetramercaptopropionate (PETMP). Real-time reaction kinetics (NIR), mechanical properties (three-point bending) and polymerization stress (tensometer) were evaluated.

Results and Discussion

Dynamic shrinkage basically increases linearly with respect to conversion over the majority of an isothermal polymerization process. However, the reaction exotherm and irradiative heating due to the curing light contribute to alter the shrinkage profile, as shown for photopolymerizations of triethylene glycol dimethacrylate as a model dimethacrylate (Figure 2). In addition, there is good evidence for a delay in shrinkage relative to conversion beyond approximately 50% conversion as the material enters the glassy state. The highest polymerization rate (highest DMPA concentration) resulted in the highest conversion but lowest shrinkage within this series, which is the reverse of the predicted theoretical volumetric shrinkage based only on conversion. Therefore, in practical terms, dimensional change during the photopolymerization process is not simple and real-time effective temperature data, rather than just cure temperature, is required to better understand the chemical and physical changes taking place during the photopolymerization process.

With higher initiator concentration, polymerization is more rapid and generates a greater exotherm. The

monomer displays a significantly higher coefficient of thermal expansion compared with the crosslinked polymer which, in part, may explain the inverse relationship between reaction rate and conversion-dependent shrinkage. Efforts currently underway to obtain mechanical property data with respect to conversion during polymerization have produced good modulus profile results with the rheometer but a relatively poor coupled NIR signal. In contrast, the NIR optical access through the photo-DMA is excellent, but the proper conditions to achieve acceptable modulus data between parallel quartz plates operating in single cantilever shear mode are still being developed. Prior work by other investigators using rheometry with simultaneous NIR have produced good results.^{5,6}

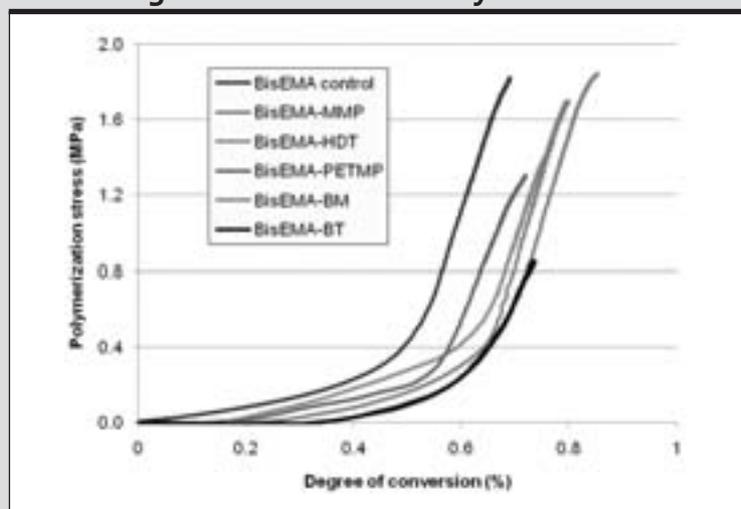
Our laboratory has previously reported on tensometer-based photopolymerization stress measurements combined with conversion.⁷⁻⁹ As a current demonstration of this analytical technique, as well as an

effort to reduce the final stress in the polymer on the basis of delayed gelation, the photopolymerization of BisEMA was conducted in the presence of a 10-to-1 mole ratio of methacrylate groups to the different thiol chain transfer agents used. Thiol addition suppressed autoacceleration and delayed vitrification (kinetic conversion versus time data not shown here). Compared with the control, significantly higher final conversion was achieved along with increased modulus. Depending on the thiol functionality and chain transfer reactivity, polymerization stress was either similar to or greatly reduced relative to the BisEMA control (Figure 3).

Normally, either higher conversion or higher modulus would contribute to an increase in the final stress level. All the thiol-modified polymerizations show a delay (with respect to conversion) in the onset of stress development, which is expected with delayed gelation, as well as delayed vitrification. The most reactive thiol evaluated here, benzene thiol, shows the greatest

FIGURE 3

Polymerization stress development versus conversion for BisEMA modified with a series of thiol chain transfer agents at a 10:1 methacrylate to thiol ratio



potential to delay gelation and reduce the final stress state. This simple chain transfer approach dramatically changes the polymer network structure but produces a material with excellent mechanical properties and a lower content of extractibles. Alternative stress reduction mechanisms can be considered, but the use of coordinated conversion measurement along with polymer property evolution monitoring clearly provides a useful method to rationally evaluate specific stress reduction pathways. ▀

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