

## POLYMERIZATION SHRINKAGE MEASUREMENTS OF PHOTOCROSS-LINKED DIMETHACRYLATE FILMS

Sheng Lin-Gibson, Forrest A. Landis, and Christopher M. Stafford

Polymers Division, National Institute of Standards and Technology  
Gaithersburg, MD 20899-8540

### Introduction

Photopolymerized di(meth)acrylates are widely used in coatings, adhesives, and dental materials.<sup>1</sup> While significant improvements have been made over the past several decades, polymerization shrinkage and associated polymerization stress remain a challenge. To understand the polymerization shrinkage/stress problem and its effects on various material properties, facile characterization techniques are needed. Mercury dilatometry is generally considered to be the most accurate; however, it is labor intensive to perform and not readily available. Shrinkage values obtained from various test methods, including volumetric shrinkage measurements (pycnometry, dilatometry, etc.) and linear shrinkage measurements (microscopy, interferometry, etc.) can be different for the same materials. Furthermore, polymers measured using the same technique performed by different laboratories can differ significantly.<sup>2</sup> These discrepancies arise not only from the inherent differences in the measurement techniques, but also from the difficulties in preparing consistent samples. For example, depending on the test method, it may be very difficult to cure the polymer using the same light source and intensity. Differences in reaction conditions may result in variations in conversion, polymer structure, and ultimately, different amounts of polymerization shrinkage. It is not surprising that with these complexities in shrinkage measurements, it is difficult to relate shrinkage results to other polymerization properties. As noted in a recent article, there is a tremendous need for a "test suite" from which multiple material properties can be characterized.<sup>3</sup>

We are currently developing combinatorial and high-throughput based test suites to meet these objectives. Our recent work focused on the preparation of two-dimensional (monomer composition and irradiation time) gradients and the characterization of polymerization conversion, mechanical properties, and biocompatibility.<sup>4</sup> In the current work, we aim to expand our testing capabilities to include polymerization shrinkage using FTIR (Fourier transform infrared) spectroscopy, interferometry, and confocal microscopy as complementary techniques.

### Experimental

**Materials.**<sup>†</sup> The base monomer 2,2-bis[4-(2'-(hydroxyl-3'-methacryloxyprop-oxy)phenyl)propane (BisGMA), and diluent monomer triethylene glycol dimethacrylate (TEGDMA) were obtained from Esstech Inc. Camphorquinone (CQ) and ethyl 4-N,N-dimethylaminobenzoate (4E) were purchased from Aldrich Corp. All reagents were used as received.

**Fabrication of photo cured films.** BisGMA and TEGDMA were mixed at a 60:40 mass ratio. The resin mixture was activated for visible light photopolymerization with 0.2 % CQ and 0.8 % 4E (by mass) and stored in the dark until use.

For the preparation of films, a 25  $\mu\text{m}$  metal shim, a commercial polyester film (thickness  $\approx 45 \mu\text{m}$ ), and a polyimide film (thickness  $\approx 60 \mu\text{m}$ ), were used as spacers in order to obtain films of various thickness. With the spacer in place, the BisGMA-TEGDMA mixture was sandwiched between two glass slides and polymerized in a visible light curing unit (Triad 2000) for 1 min per side with the turntable on. All samples were characterized 24 h after irradiation to allow for complete cure.

**FTIR Spectroscopy.** The FTIR spectra of the uncured and cured resin were obtained using a Nicolet Magna 550 FT-IR spectrometer (Madison, WI) configured with a white light source, a  $\text{CaF}_2$  beam splitter, and an InSb

<sup>†</sup> Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the material and the equipment identified is necessarily the best available for the purpose.

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detector. The IR spectra in the region of  $4000 \text{ cm}^{-1}$  to  $650 \text{ cm}^{-1}$  were acquired from 64 co-added scans at a  $4 \text{ cm}^{-1}$  resolution. FTIR spectra of neat resins were obtained by sandwiching the resin mixture between KBr salt plates with a spacer of known thickness. Alternatively, FTIR of resin films thinner than  $15 \mu\text{m}$  were spin coated onto a silicon wafer and the thickness was confirmed by interferometry.

**Confocal Microscopy.** Confocal optical microscopy analysis of the cured films was carried out using a Zeiss LSM 510 laser scanning confocal microscope with a 1 Airy unit pinhole in reflectance mode. A 633 nm laser was used to examine the cross-sectional thickness of the films using a 50X magnification objective. Five points were examined per sample to determine the uniformity of the film thickness. The relative uncertainty associated with the confocal microscopy is estimated to be 5 %.

**Interferometry.** The thickness was determined using UV-visible interferometry (Model F20, Filmetrics, Inc.) operated in reflectance mode with a spot size of  $\approx 0.5 \text{ mm}$  and an acquisition time of a few seconds. The spectra were fit using the reflectance data between 500 nm and 800 nm using the refractive index for an acrylic polymer. Five data points were obtained for each film for statistical analysis. The relative uncertainty for all measurement techniques is estimated to be less than 5 %.

### Results and Discussion

The current study uses interferometry, FTIR spectroscopy, and confocal microscopy as complementary techniques to determine the polymerization shrinkage of photopolymerized dimethacrylates. These measurement techniques fit well with our existing combinatorial platforms from which polymerization conversion, mechanical properties, and biocompatibility can be obtained.<sup>4</sup>

All of the aforementioned characterizations require film samples. To make the current measurement technique applicable to existing capabilities, the film thickness has to be optimized such that all measurements were conducted in the bulk regime. The basic idea for the current polymerization shrinkage measurements involves confining volumetric shrinkage to one-dimension (Figure 1). This assumption is valid for films that have a large aspect ratio in their surface area to thickness. In the schematic shown, the volume of the resin is  $V_0 = \pi r^2 h_0$  and the volume of the polymerized film is  $V = \pi r^2 h$ , where  $r$  and  $h$  are the radius and thickness, respectively. The volumetric shrinkage is therefore directly proportional to changes in the film thickness. Such geometry also allows multiple characterization techniques to be carried out for measuring the film thickness.

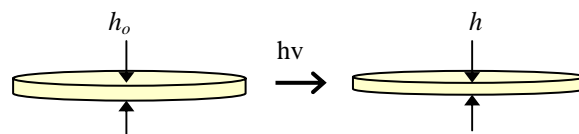


Figure 1. Schematic showing the volume before and after polymerization

Interferometry is a well-established method for determining the thickness of thin films. Previous work has shown that interferometry can be used to effectively follow the reaction conversion (based on changes in the sample refractive index upon polymerization) and polymerization shrinkage.<sup>5</sup> Using confocal microscopy, the cross-sectional thickness of a free-standing film can be measured accurately. In addition to edge-on measurements, confocal microscopy can also be used to estimate the thickness of a film on a substrate if the refractive index of the film is known. This technique involves measuring the distance that the focal point of the objective moves from the surface of the film to the film/substrate interface. This approach can be particularly useful for liquid resins.

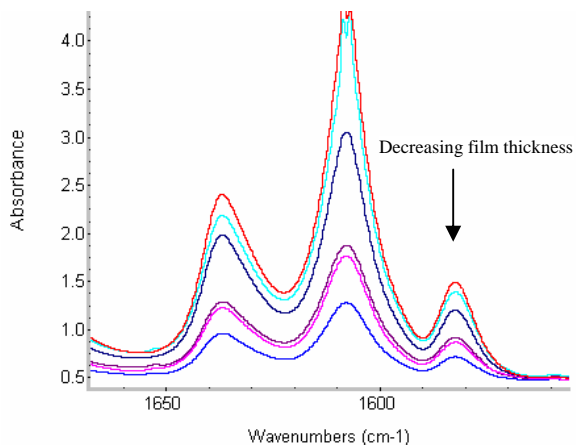
FTIR has been widely used to monitor the reaction conversion for these types of photo-polymerizations; however, to our knowledge, little has been reported regarding using FTIR to determine the polymerization shrinkage. The Beer-Lambert law states that

$$A = \epsilon bc \quad (1)$$

where  $A$  is the absorbance,  $\epsilon$  is the molar absorptivity or extinction coefficient,  $b$  is the path length of the sample (or effectively, the thickness of the sample), and  $c$  is the concentration of the compound. The concentration  $c$

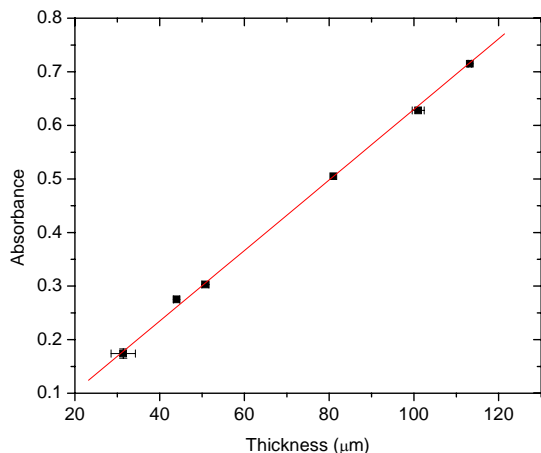
is constant for a given photopolymerization. The extinction coefficient, which is dependent on the refractive index of the material, changes slightly with polymerization. Since the current work focuses on the thickness variation over a relatively small conversion range, it is reasonable to assume that small variations in the extinction coefficient are negligible. Thus, it is possible to determine the thickness of a sample via the Beer-Lambert law using FTIR spectroscopy.

The first experiment involves a validation study in which BisGMA-TEGDMA resins and films of different thickness were prepared and characterized by interferometry, FTIR, and confocal microscopy. Spacers of different thickness were used to control the film thickness and all the films were cured under identical conditions. For these materials, the concentration and extinction coefficient are identical, rendering the film thickness the only variable. Figure 2 shows the region of interest of the IR spectra for the polymerized films. The methacrylate C=C absorption at  $1637\text{ cm}^{-1}$  and the aromatic absorption at  $1583\text{ cm}^{-1}$  clearly increase as the film thickness increases. Of the two absorption bands, the aromatic peak is preferred for thickness determination, since this peak does not change with polymerization and is often used as an internal standard.



**Figure 2.** Absorbance spectra for polymerized BisGMA-TEGDMA films of varying thicknesses

The thickness of each film was independently measured using confocal microscopy, which precisely measures the film cross-sectional thickness. The relationship between the film thickness and absorbance is plotted in Figure 3. A film of an unknown thickness at the same composition and conversion can thus be obtained from the measured intensity using this calibration curve.



**Figure 3.** Absorbance versus thickness for BisGMA-TEGDMA films. The thickness was determined using confocal microscopy. The error bar for the absorbance axis is smaller than the size the symbol; the error bar for the thickness is shown. Line drawn is a linear fit of the data.

The experiments for the resin were conducted in a similar manner. The absorbance versus thickness curve looks comparable to those of the polymerized film (data not shown). With these two calibration curves in hand, it is possible to determine the film thickness before and after photopolymerization. Our preliminary results show great promise. Experimental details are currently being analyzed to greatly enhance the accuracy of these measurements.

## Conclusions

A “test suite” is being developed from which a number of properties, including polymerization shrinkage, can be determined. The polymerization shrinkage was determined by confining the shrinkage to one-dimension and thus the thickness change is directly proportional to the volumetric shrinkage. Preliminary tests show the feasibility of this measurement approach. Detailed data and statistic analysis will be presented.

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