

Rational design of photopolymer materials for holographic data storage

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1. INTRODUCTION

Photopolymer material performance is a key aspect of any holographic data storage system, but design of a formulation is daunting in the face of nearly unlimited choices of chemical components. A popular general strategy is to separate passive and active functions through the use of two orthogonal polymer chemistries that can be optimized independently: a thermo-set host matrix, and a photo-addressed writing chemistry. The host matrix generally determines bulk properties such as modulus, background index, and environmental stability; while the writing monomer is independently chosen to have high index contrast with the matrix (which increases M/#) and low molecular weight (for rapid diffusion).

The design process of the material is ideally informed by rational and quantitative guidelines rather than trial and error. Here we describe a systematic approach to the design of these materials that includes a predictive response model with independently measured parameters. An upper bound for the maximum index change, typically the primary specification for such materials, is established and non-idealities that prevent reaching this bound are found.

2. THE FORMULATION LIMIT ON M/#

Total available index change is typically experimentally determined for any holographic polymer as quantified by the M/#, measured via the superposition of many weak Bragg gratings. However, the maximum index contrast the material will support can be quantified via bulk index measurements of uniformly cured samples of various monomer loadings. From these measurements, the indices of matrix and dissolved writing monomer, respectively, can be inferred. Then, assuming that the matrix swells during recording so that free volume is conserved, the theoretically achievable M/# is readily calculated via the Lorentz-Lorenz law for any formulated monomer concentration.

This upper limit is useful because, for many formulations of practical and commercial interest, the M/# as measured by holographic recording is found to be a factor of 2 to 8 lower (fig. 1). This discrepancy must be attributed to non-ideality of the media's response to exposure, potentially including: nonlinearity of the radical generation rate with intensity; low fidelity response due to strong reaction/diffusion coupling; change of reaction or diffusion constants with degree of polymerization; and/or poor confinement of mobile species. This motivates a detailed development model that can be used to identify and guide strategies to alleviate such problems.

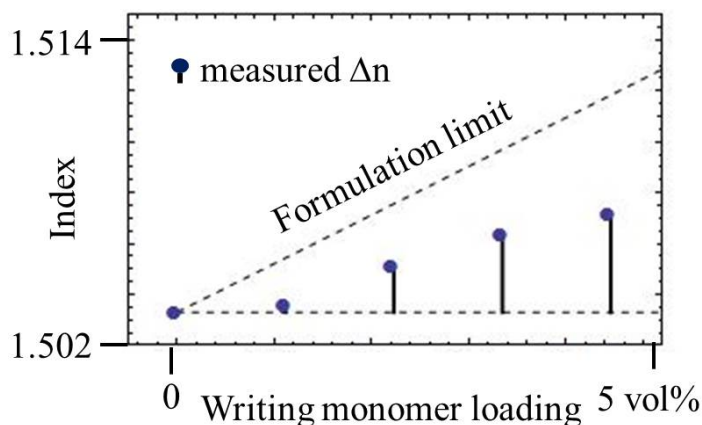


Figure 1. Measured holographic index contrast falls short of the theoretical upper bound given by the “formulation limit”, due to non-ideality of the index response to exposure. Bulk prism coupler index (dashed line), total index contrast from holographic M/# (symbols).

3. PREDICTIVE HOLOGRAPHIC POLYMER DEVELOPMENT MODEL

In order to understand these non-ideal behaviors (and how they might be reduced, in order to bring the practically achievable M/# closer to its theoretical maximum) we first develop a numerical model of the photopolymerization kinetics. This model consists of a coupled set of differential reaction/diffusion equations, with a small number of rate constants whose values are characteristic of the particular media formulation.

These rate constants are, in general, difficult to measure independently, because reaction/diffusion processes tend to be highly coupled and take place over similar time scales. Additionally, the structures are small (~1 micron) and weak (~1% concentration variations), defeating many traditional polymer characterization methods such as FTIR. One well-established solution, exemplified in the work of Sheridan et al, is to simultaneously fit a large number of unknown rate constants to a single observed quantity: the growth of a grating's fundamental spatial harmonic as a function of time. Our approach is fundamentally different and thus could potentially complement Sheridan et al's approach by providing independent verification of rate constants. We measure each rate constant separately in an experiment that decouples its time scale from the time scales of other processes. Briefly, index development from concentration is measured via prism coupler as shown in Figure 1, radical generation is calculated ab initio from published photoinitiator data, diffusion rates are measured via gravimetric analysis and propagation and termination kinetic constants are measured from Bragg grating development. The differential equations are integrated numerically in real-space with no harmonic assumption.

4. RESULTS AND CONCLUSION

We apply this general approach to a novel high-performance two-chemistry photopolymer. After independently obtaining all model parameters, we validate the entire model by testing it in different regimes. First, we study the effect of monomer species and loading on M/# to test the capability of the model, derived only from weak consumption measurements, to the complete consumption of monomer. Second, we study the index profile of very large (~50 micron) features. This large scale mixes the time scales of diffusion and polymerization, leading to strong coupling; thus, it serves as a rigorous test of the model (fig. 2).

On the basis of this model, we conclude that the most significant contribution to loss of M/# is unwanted diffusion of active radicals into the dark fringes of a grating. This insight provides guidance for the improvement of holographic formulations. In addition, the predictive upper bound on material dynamic range enables selection of formula refractive indices and concentrations to meet particular M/# requirements. Independent tests of monomer diffusivity and polymerization rate guide selection of molecular weight, reactivity and matrix glass transition temperature. Thus, a systematic approach to the selection and formulation of the material becomes possible.

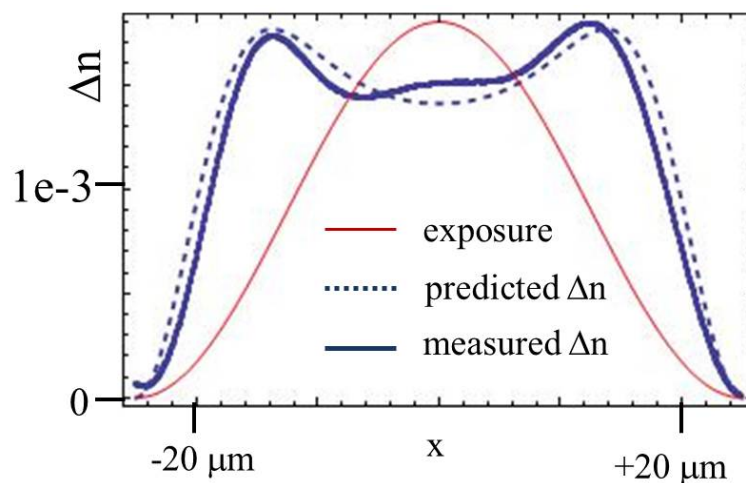


Figure 2. Index profile from ~50 μm sinusoidal illumination. The model correctly predicts the index response, even when that response is highly non-ideal due to strong reaction/diffusion coupling.