Epoxy Resin−Photopolymer Composites for Volume Holography

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Efficient materials for recording volume holograms are described that could potentially find application in archival data storage. These materials are prepared by mixing photopolymerizable vinyl monomers with a liquid epoxy resin and an amine hardener. A solid matrix is formed in situ as the epoxy cures at room temperature. The unreacted vinyl monomers are subsequently photopolymerized during hologram recording. A key feature of these materials is the separation of the epoxy and vinyl polymerizations. This separation allows for a large index contrast to be developed in holograms when components are optimized. The standard material described in this work consists of a low index matrix ($n \cong 1.46$), comprised of diethylenetriamine and 1,4-butanediol diglycidyl ether, and a high index photopolymer mixture ($n \cong 1.60$) of *N*-vinylcarbazole and *N*-vinyl-2-pyrrolidinone. This material is functional in thick formats (several millimeters), which enables narrow angular bandwidth and high diffraction efficiency. A dynamic range (M/#) up to 13 has been measured in these materials. Holographic performance is highly dependent on the amount of amine hardener used, as well as on photopolymer shrinkage.

Introduction

Photopolymers have been extensively investigated as holographic recording media for several decades[1−3] for many applications, including holographic scanners,[4,5] LCD displays,[6,7] helmet-mounted displays,[8] optical interconnects,[9−11] waveguide couplers,[12] holographic diffusers,[13−15] laser eye protection devices,[16] automotive lighting,[17] and security holograms.[18,19] Materials adequate for commercial application in archival data storage, however, have not yet been developed. Holograms (data) are stored in photopolymer materials as spatial modulations of refractive index created in response to an interference pattern generated by incident laser beams. Because of photoreactions, the refractive index of irradiated areas of a material differs from that of dark areas. The larger the refractive index difference between these two regions, the greater the data storage capacity of the material. The storage capacity of the material is also enhanced if the medium is thick (1−5 mm), as this enables recording of many holograms in a given volume of material and results in improved diffraction efficiency of the phase grating (modulated index).[20,21] To achieve the desired storage capacity that would make holographic data storage commercially viable ($\sim$100 bits/μm^2)[21] will therefore require developing a large index contrast in thick photopolymer materials.

Large index modulation is difficult to achieve, however, with holographic materials formed entirely of photopolymers. Distinctly separate polymerization of different low and high index monomers (typically vinyls) is required to develop large index contrast in such materials. To the extent that these monomers copolymerize, a polymer possessing an averaged index forms and the index contrast is diminished. Considerations of resonance stabilization and polarization factors for vinyl radicals[22] in conjunction with the Alfrey−Price equations[23] indicate that some copolymerization is unavoidable, meaning storage capacity in such photopolymer materials is limited. Nevertheless, entirely photopolymeric storage materials allow for the convenient forma-

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tion of thick films with high optical clarity (a necessary condition for holographic data storage).

Much better index contrast should be possible if the low and high index components of a material are not formed simultaneously via the same chemistry. One simple way to accomplish this is to mix photopolymerizable monomers with an inert, preformed polymer and modulate the index between these two components. Most of the photopolymer-based holographic materials now available commercially are of this type.[24] The preformed polymers in these materials, however, were not originally intended to provide refractive index contrast. Rather, they served as "binders" imparting physical characteristics that allowed the unexposed materials to be handled and stored as dry films prior to hologram formation.[3] That the binder could participate in hologram formation was not established in the literature until a report by Smothers et al. in 1990.[24] Since then, the implementation of preformed polymers for the purpose of maximizing index contrast has been investigated with some very promising results.[25-28]

This strategy, however, is not ideal. If the binder is a solid polymer, then complicated processing is required: generally, the polymer and monomers are mixed in a solvent that is evaporated during film deposition. This process practically limits the film thickness ($\leq 100 \, \mu$m), and therefore storage capacity, of a material. Much simpler, solventless processing is possible if a fluid polymer is used as a binder, and photopolymerizable monomers are simply mixed in.[25] In this case, however, initially developed index modulation is erased by mass transport in the fluid until the material sets up sufficiently to limit this transport. A prerecording photoexposure can be applied to thicken the mixture prior to hologram recording, but the maximum achievable index contrast is diminished nonetheless. The initially formed photopolymer becomes in effect part of the binder either way, hence lowering the overall contrast between the binder and the unreacted photopolymer.

We have prepared holographic materials by an alternative strategy that eliminates these problems.[29] Rather than using a preformed polymer, a solid binder (or matrix) is formed in situ by a room temperature curing reaction. This method allows for the convenient preparation of thick films (several millimeters) in contrast to strategies which implement solid binders. These materials are comprised of polyamine-hardened epoxy resins containing vinyl monomers. Varying the ratio of amine to epoxy adjusts the cross-link density of the matrix and thereby affords control over mechanical properties, hence allowing optimization of holographic performance. We note that the holographic performance of materials prepared by similar strategies have recently been reported,[20,30,31] and that this class of photopolymers

exhibits the highest dynamic range (M/#)[32] demonstrated to date (42 in a 1 mm thick film[20]).

Experimental Section

Materials and Equipment. 1,4-Butanediol diglycidyl ether (BDGE, $n = 1.4530$), 1,2,7,8-diepoxyoctane (DEO, $n = 1.445$), diethylenetriamine (DTA, $n = 1.4826$), bis(4-glycidyloxyphenyl)methane (GPM, $n = 1.579$), *m*-xylylenediamine (XDA, $n = 1.571$), and *N*-vinyl-2-pyrrolidinone (NVP, $n = 1.5112$) were purchased from Aldrich and used as received. Epoxypropoxypropyl-terminated poly(dimethylsiloxane) of 1 centistoke viscosity (EPS1, $n = 1.446$), 70% *tert*-butyl hydroperoxide in water (TBHP), and Irgacure 784 radical photoinitiator (PI) were obtained from Gelest, Acros, and Ciba-Geigy, respectively, and were also used as received. *N*-Vinylcarbazole (NVC, $n = 1.68$) was purchased from either Aldrich or Fluka and sometimes needed to be purified (to remove an insoluble fraction), in which case it was dissolved in ethyl acetate, filtered, and then dried in vacuo. The amine hardeners were stored under nitrogen, while NVC, NVP, and TBHP were refrigerated (4 °C).

Near-IR spectroscopy (1.2–2.5 μm) was performed on a Nicolet Magna-IR 760 with a white light source, a CaF$_2$ beam splitter, and a PbSe detector. A long-pass filter (at 630 nm) was used to reduce the photoexposure of the sample by the FTIR. ^{1}H NMR was conducted on a Bruker Avance 400 MHz spectrometer.

Photopolymer Mixtures. The desired weight quantities of the NVC and NVP monomers were weighed into a brown bottle. Photoinitiator was then added in a quantity totaling 3% of the combined weight of the monomers. Finally, TBHP was added in a quantity totaling $^{1}/_{5}$ of the photoinitiator weight, and the mixture was vigorously stirred. The purpose of the TBHP is to prevent a colored titanium complex from forming upon photoinitiator decomposition. Mixtures were prepared and handled under red light and stored in a refrigerator (4 °C).

Epoxy/Photopolymer Formulations. Formulations were prepared by mixing volume quantities (or weight quantities in the case of GPM) of the constituents in the following order: epoxy resin, amine hardener, photopolymer mixture. These formulations were evacuated 30–60 min (10^{-2} Torr) to remove dissolved gases that result in bubbles during epoxy solidification. All formulations were prepared under red light and stored in the dark while the epoxy cured at room temperature. The usual formulation volume was 5 mL in this study.

Sample Preparation. To form optical films, several drops of a formulation were placed between two 75 × 50 × 1 mm glass plates separated by stainless steel spacers of the desired thickness (0.2–2.2 mm). These films were prepared when formulation viscosity was sufficient to counteract spreading of the drops on the glass slides. GPM/XDA cures rapidly, so samples were prepared about 5 h after mixing, whereas DEO/DTA samples could only be formed after ~48 h. The time for preparing samples depended on epoxy-to-amine ratio, volume percent photopolymer, and the formulation volume.

Hologram Recording. Holographic exposure was begun without any preimaging exposure once the epoxy matrices solidified. Output from a Coherent frequency-doubled Nd:YAG laser (model DPSS-532) at 532 nm was spatially filtered and collimated to provide the holographic exposures. The reference and signal beams were 11 and 6 mm in diameter respectively to ensure that the signal beam was within the reference beam at all sample rotations. The irradiation of each beam was 2 mW/cm^2, and samples were exposed for a total of 1500 s providing total holographic exposures of 1695 mJ. Thirty

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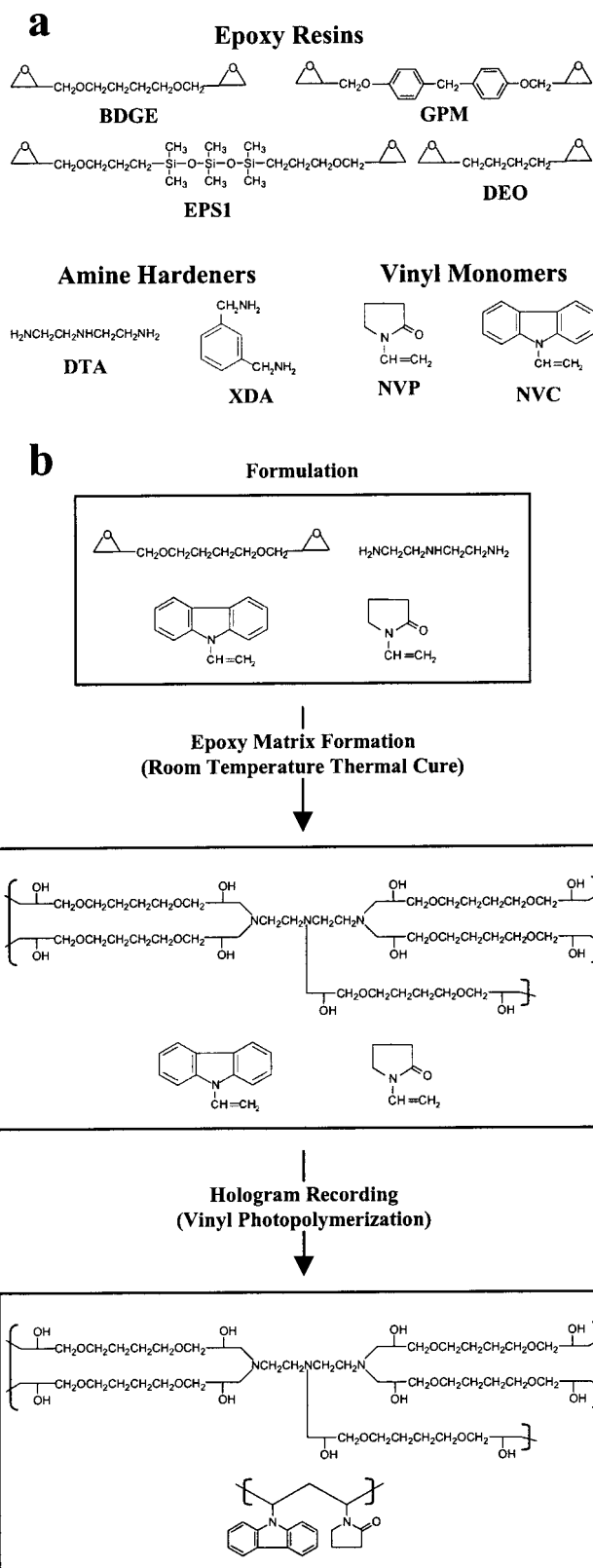(32) Mok, F.; H.; Burr, G. W.; Psaltis, D. *Opt. Lett.* **1996**, *21*, 896.

holograms were angularly multiplexed with a 40° external angle of intersection between the two beams. The reference and signal beams remained fixed, and the sample was rotated using a computer-controlled motorized stage from Newport Corporation (model URM100PP). Exposure times were scheduled to yield near equivalent diffraction efficiencies for each hologram in a sample. Following hologram writing, the sample was allowed to rest in the dark for 5 min and then flood-cured without removal from the apparatus by a xenon light source from Oriel to complete the polymerization of any photoactive monomers and render the sample optically clear. Holograms were read out with 0.002° angular resolution and hologram intensities were measured with a Newport optical meter (model 2835C) and detector head (model 883SL). Sample shrinkage was determined by measuring the Bragg detuning of the holograms at the reference beam only.[33,34]

Results

By separating the chemistry of matrix formation from hologram recording (Figure 1), photopolymer composites with high capacities for data storage can be generated. In this work, a nonphotoactive matrix, an epoxy, was combined with up to 25% (v/v) of photopolymerizable vinyl monomers. The constituents were chosen to deliver a large refractive index contrast to developing holograms. In our standard materials, a low index epoxy matrix, diethylenetriamine (DTA) hardened 1,4-butanediol diglycidyl ether (BDGE) ($n \cong 1.46$), was paired with a mixture of two high index photopolymers, N-vinylcarbazole (NVC) and *N*-vinyl-2-pyrrolidinone (NVP) ($n \cong 1.60$). The resulting materials were efficient storage materials for volume holograms. Figure 2a demonstrates that 30 angularly multiplexed holograms could be recorded in a 0.25 mm thick sample containing 15% (v/v) photopolymer. The performance value that characterizes the capacity of these materials, the dynamic range (M/#),[32] can be calculated from these data by summing the square root of the diffraction efficiency of each hologram. The M/# determined for this sample was 5.76.

One important feature of the data shown in Figure 2a is the nearly equivalent hologram strengths in the series. This was the result of a scheduling process,[35] in which holograms recorded earlier had less exposure than those recorded later. The suitability of these samples to scheduling demonstrates that sample reactivity can be predicted and controlled. The average diffraction efficiency of these holograms is 3.70%. Figure 2b shows the visible exposure curve for recording these holograms. 1695 mJ of 532 nm light essentially exhausted the dynamic range of this sample, which is typical for these epoxy-based materials.

Because these materials have high optical clarity and a modest absorption cross-section at 532 nm (Figure 3), thick samples can be readily prepared.[36,37] Figure 2c shows 30 holograms encoded in a 2.33 mm thick sample containing 5 vol % photopolymer. The angular bandwidths of these holograms are clearly much narrower than those observed in the 0.25 mm thick sample shown in Figure 2a. As expected, the hologram bandwidth
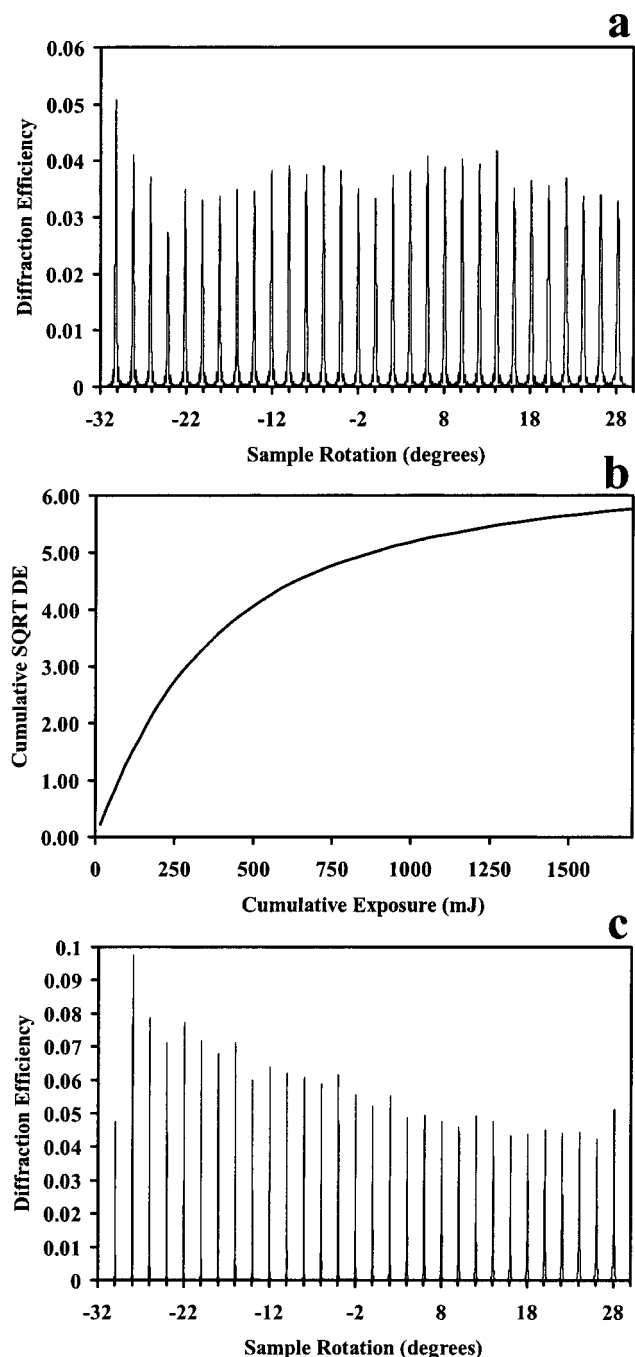
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a

Epoxy Resins

BDGE   GPM

EPS1   DEO

Amine Hardeners   **Vinyl Monomers**

DTA   XDA   NVP   NVC

b

Formulation

Epoxy Matrix Formation
(Room Temperature Thermal Cure)

Hologram Recording
(Vinyl Photopolymerization)

Figure 1. (a) Chemical structures of the various formulation constituents (excluding photoinitiator and TBHP) examined in this study. (b) Scheme illustrating the two separate steps of matrix formation (here, BDGE/DTA) and photopolymerization. The fully cross-linked epoxy matrix that would be anticipated from a 1:1 N−H to oxirane mole ratio in the initial formulation is depicted. Generally a 2:1 ratio was used in this study.

decreases with sample thickness.[38] Thus, the 0.25 mm sample has an angular bandwidth (fwhm of the 0°

Figure 2. (a) Diffraction efficiency vs sample rotation for 30 holograms written in a 0.25 mm thick sample of BDGE/DTA containing 15% (v/v) NVC/NVP photopolymer. (b) Cumulative square root of diffraction efficiency vs cumulative exposure (mJ) for the sample in a. Note that the dynamic range has not completely leveled off at the end of exposure. It is possible to fully exhaust the sample capacity with extended exposures that were deemed impractical. Approximately 90% of total capacity was used in most samples. (c) Diffraction efficiency vs sample rotation for 30 holograms written in a 2.33 mm thick sample of BDGE/DTA containing 5% (v/v) NVC/NVP.

hologram) of 0.215° while the 2.33 mm sample has a bandwidth of 0.030°. Diffraction efficiency per hologram also increases in thicker material. The average diffraction efficiency of holograms in the 2.33 mm sample (5.72%) is greater than that observed for the thinner sample (Figure 2a) despite a much smaller proportion of photopolymer. The M/# calculated for this thicker sample is 7.13. These data illustrate the benefits of
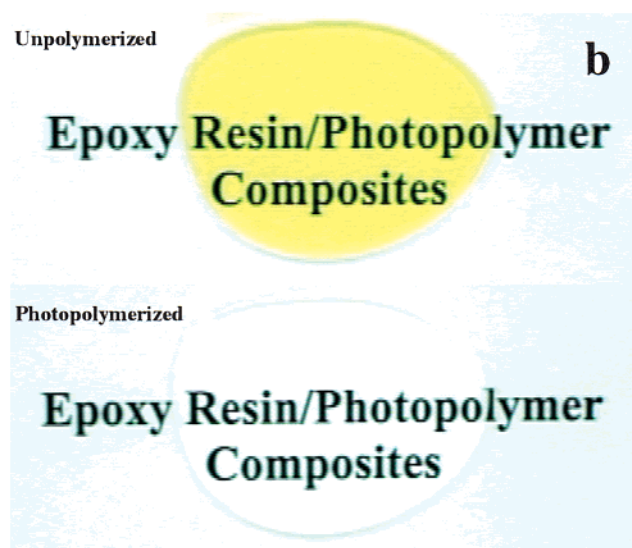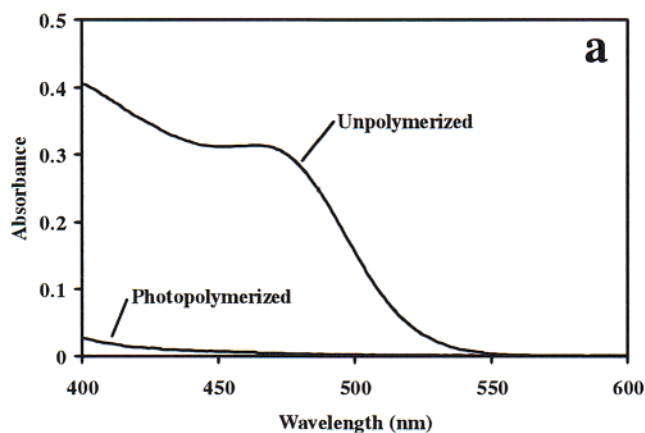

Figure 3. (a) UV–vis absorption spectra for a 0.25 mm thick sample of BDGE/DTA (containing 15% NVC/NVP) obtained both prior to and following photopolymerization. (b) CCD images of a comparable sample taken both prior to and following photopolymerization.

working with thick holographic recording materials: not only is the dynamic range enhanced due to increased diffraction efficiency, but also holograms can be densely packed into the material because of their narrow angular bandwidths.[39]

Although thicker samples perform better than thinner materials, their holograms are much more sensitive to dimensional changes in the sample. This limits their recording capacity as the shrinkage due to photopolymerization can cause significant detuning (shifting of hologram positions during encoding) and distortion of the holograms.[38,39] It is apparent in Figure 2c, particularly in the last few holograms written (positive rotation angles), that some distortion is present despite a low volume fraction of photopolymer. This results in inaccurate data readout and diminished dynamic range. For thicker samples, then, photopolymer content has to be reduced to limit shrinkage. Figure 4 illustrates the shrinkage-induced distortion that arises from the interplay of thickness and photopolymer content. No distortion was observed for up to 15 vol % of NVC/NVP

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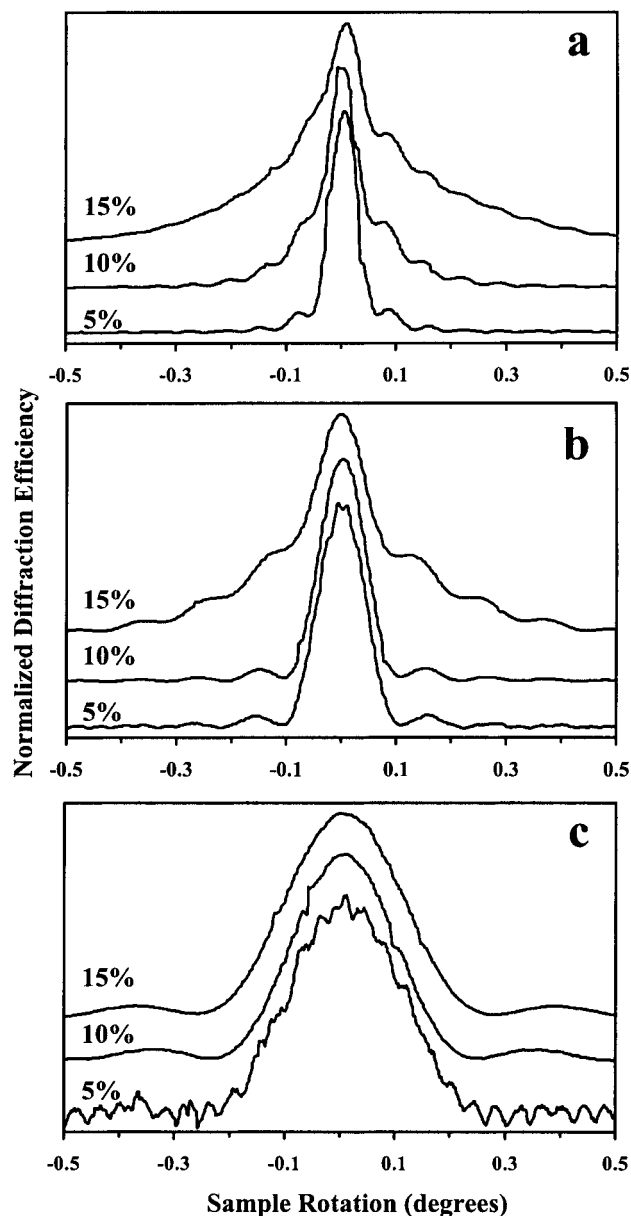
Figure 4. Angular response curves for holograms written in BDGE/DTA materials of variable sample thickness containing 5, 10, and 15% (v/v) NVC/NVP: (a) 1.0 mm thick, (b) 0.5 mm thick, and (c) 0.25 mm thick. Note that 30 holograms were written in each sample, but only the 0° hologram was shown for clarity. Further, diffraction efficiencies were normalized to a peak of 1 for all samples (consequently, noise is apparent for samples exhibiting low diffraction efficiency, i.e., the 5%, 0.25 mm thick sample). Distortion (manifested by uplifted nulls) was clearly magnified by both increased photopolymer level and sample thickness, each of which leads to greater photopolymerization shrinkage.

in BDGE/DTA when sample thickness was only 0.25 mm, but at 1 mm, slight distortion had onset even with 5% photopolymer. By varying thickness and photopolymer volume fraction, an M/# as great as 13.0 was achieved in this study (a 1.5 mm thick sample with 10% NVC/NVP), but the holograms in that sample were distorted.

It should be noted that the M/# values reported in this study are dependent on the delay time between hologram recording and initial material formulation.
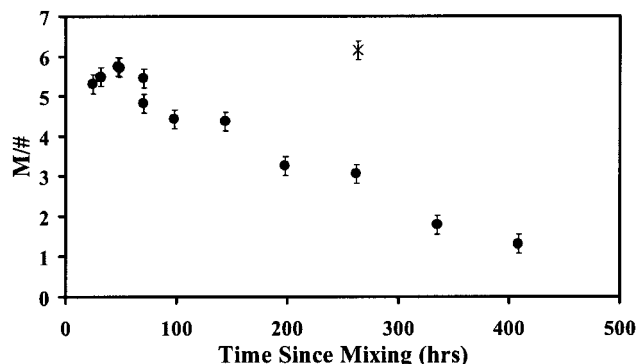
Figure 5. Sample dynamic range (M/#) plotted as a function of the time between formulation and holographic exposure. Multiple samples were prepared concurrently, and then exposed periodically in turn. Samples were stored in the dark at room temperature prior to exposure except for the sample represented by ×, which was refrigerated (4 °C) after an initial 48 h at room temperature. This sample exhibited a dynamic range as if it were only 48 h old even though 264 h had elapsed since mixing. Note that chilled samples were allowed to reequilibrate to room temperature prior to exposure.

Figure 5 shows the gradual diminution of dynamic range realized as encoding time was postponed. This aging process could be arrested by storing the samples (after the epoxy had cured) at 4 °C. These samples could then be encoded with holograms weeks after initial formulation without any degradation in their recording performance.

Discussion

A necessary condition for achieving maximum holographic recording performance in epoxy−photopolymer composite materials is the complete separation of the epoxy curing process from the polymerization of the vinyl monomers. If these two reactions occur simultaneously, then the two polymers mix before recording and the refractive index contrast is reduced due to mixing of low and high index components. To ensure complete and rapid formation of the epoxy matrix, polyamine hardened epoxies were used. These materials allow for in-situ matrix formation because the chemistry proceeds quickly at room temperature.[40] In addition, there is a wide range of economical resins and amines to choose from allowing for optimization of holographic performance. We note that other epoxy chemistries, which rely on thermal polymerization schemes,[40] may not be as well suited for this application because the heat may also induce some polymerization of the vinyl monomers.

The photopolymerizable monomers chosen needed to be compatible with these epoxies, i.e., they needed to be fully miscible with and chemically inert to the epoxy matrix at all stages of processing. Acrylates were not viable choices because they are known to undergo Michael-type addition with primary or secondary amine hardeners.[41] NVC and NVP, however, are not known to undergo this or other side reactions with BDGE or

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DTA at room temperature.[42] Further, previous studies on single-component materials (materials comprised entirely of photopolymers) indicated that these are good photopolymers for holography.[39,43]

Both NMR and near-IR spectroscopy support the expectation that the epoxy and vinyl polymerization reactions are separated in these systems. Various combinations of NVP, NVC, BDGE, and DTA were mixed and heated to 50 °C for 22 h, using deuterated benzene as internal lock solvent. The only reaction evidenced was the desired matrix-forming reaction between BDGE and DTA. Near-IR peaks at 1.65, 2.02, and 1.62 μm corresponding to epoxy (oxirane),[44] amino,[45] and vinyl groups,[46] respectively, were also monitored during matrix formation and hologram encoding (Figure 6).[47] Within 20 h, epoxy matrix formation was essentially complete, as the oxirane peak had disappeared and the peak arising from the amino groups had leveled off to constant intensity.[48] Little change in the intensity of the vinyl peak was observed, however, until illumination to induce photopolymerization was initiated. The slight reduction in vinyl peak intensity evident prior to illumination (roughly 15% reaction) can be attributed to some thermal polymerization of NVC/NVP, as this monomer mixture does thicken when kept for prolonged periods at room temperature. Further, matrix formation is an exothermic reaction that results in a slight elevation of formulation temperature. Note that most of the reduction in vinyl peak intensity occurred during matrix formation, not during the subsequent 28 h preceding flood illumination.

This thermal polymerization could account for the decrease in dynamic range that was observed with prolonged aging of samples at room temperature prior to hologram recording (Figure 5). To verify this, an NVC/NVP mixture was aged 216 h (9 days) at room temperature prior to formulating with BDGE/DTA. When holograms were written 2 days after formulation of the epoxy mixture, the observed dynamic range was reduced compared to that of an equivalent formulation prepared with fresh NVC/NVP. The measured value in this instance approached the level of an epoxy−photopolymer composite aged 11 days.

Given that the epoxy and photopolymer chemistries are independent, dynamic range could be expected to scale directly with the difference in refractive index between matrix and photopolymer. Systematic variation of the refractive index of one or both of these components, then, may allow for the optimization of holo-

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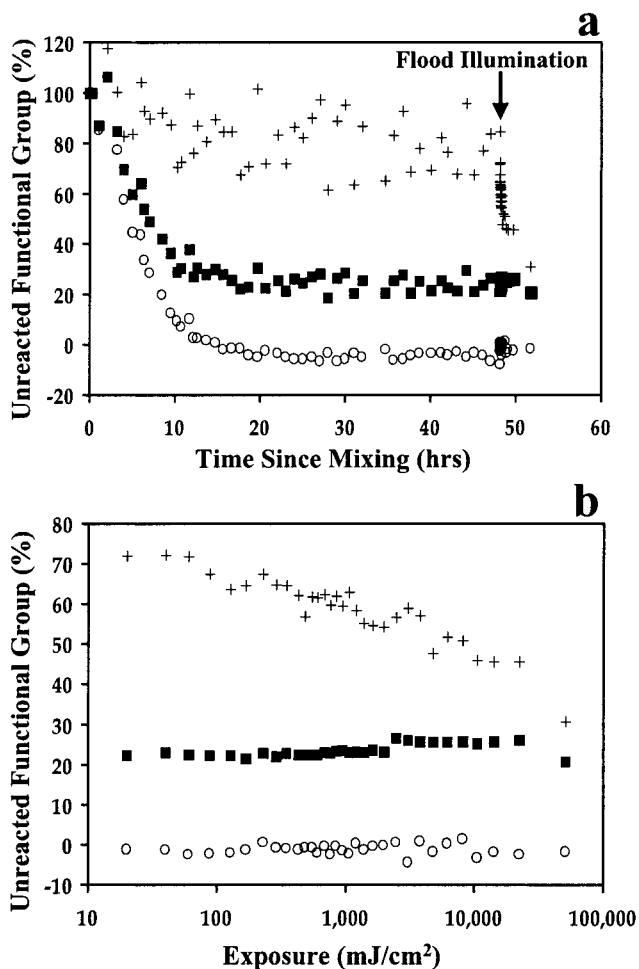
Figure 6. (a) Percent unreacted functional group remaining (determined by near-IR spectroscopy) as a function of time since formulating. Percentages were determined by the second derivative peak heights of the absorption spectra at 1.62 (vinyl, +), 1.65 (oxirane, ○), and 2.02 μm (N−H, ■). Spectra were collected periodically as the samples aged. After 48 h (the time at which holographic performance is at a maximum), the samples were exposed to a flood illumination equivalent in intensity to that used in the holographic exposures. (b) Blow-up of the photoexposure region in part a plotted as a function of illumination intensity.

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graphic recording performance. To explore this issue, the photopolymer mixture was altered. As anticipated, when the average refractive index of the photopolymer was elevated by increasing the proportion of the high index NVC, a linear increase in dynamic range was obtained. The trend breaks down at high NVC ratios because the material becomes cloudy due to phase separation. This is consistent with results reported by Dhar et al. for the incorporation of photopolymers with differing index into their matrix material.[20]

In contrast, variation of the epoxy matrix with constant photopolymer composition, did not give the expected results. The epoxy matrices investigated included DTA cured 1,2,7,8-diepoxyoctane (DEO) and epoxypropoxypropyl-terminated dimethylsiloxane (EPS1). Also, *m*-xylylenediamine (XDA) cured bis(4-glycidyloxy-phenyl)methane (GPM) was studied. On the basis of the refractive indices of these matrices, the highest dynamic range should be obtained for EPS1, while GPM should provide the lowest M/#. In reality, however, it was the EPS1 matrix that exhibited the lowest M/#, although

(42) Note that as tertiary amines, NVC and/or NVP could be expected to catalyze an epoxy ring-opening polymerization. Although this would chemically modify the epoxy matrix, little or no NVP or NVC should be incorporated since they would serve only as catalysts. The presence of more reactive protic amine hardeners such as DTA should preempt this curing mechanism. Furthermore, the steric bulk and/or low basicity of NVC and NVP should render these as poor Lewis base catalysts. See Lee, H.; Neville, K. *Handbook of Epoxy Resins*; Mcgraw-Hill: New York, 1967.

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(47) Other functional groups are not present in BDGE, DTA, NVP, or NVC that would reasonably be expected to participate in side reactions.

(48) Note that DTA is in excess so that all oxiranes should react, but unreacted N−H should remain.

Table 1. Dynamic Range for Varied Epoxy Matrices with Embedded NVC/NVP[a]

| formulation[b]	n_{epoxy}[c]	$n_{photopolymer}$[c]	M/#[d]	time recorded after mixing,[e] h
EPS1/DTA	1.4530	1.5956	0.47	74.5
DEO/DTA	1.4591	1.5956	6.21	99
BDGE/DTA	1.4621	1.5956	4.22	46
GPM/XDA	1.5551	1.5956	0.69	24

[a] All matrices contained a 50/50 mixture of NVC/NVP in a total quantity of 25% (v/v). [b] All formulations were prepared with a 2:1 ratio of N−H to oxirane. [c] Refractive indices listed are volume-weighted averages of the unpolymerized constituents. [d] M/# values are reported for 0.25 mm thick samples. [e] The recording time listed is that which yielded optimal M/# performance for each material, which varies depending on epoxy cure rate.

GPM did indeed perform poorly (Table 1). Clearly, it is not sufficient to consider merely chemical compatibility and constituent indices in evaluating potential holographic formulations.

This may be understood by considering other factors important to hologram formation, notably the mechanical properties of the matrix. Modulation of refractive index in a material during photopolymerization requires the mass transport of monomers and the movement of polymer in response to this transport. A more rigid matrix will be less able to swell, and thus will not support as much refractive index modulation. The extent of cross-linking in the matrix and the flexibility of the matrix chains between these cross-links determines the rigidity.[40] The epoxy resins used in this study were all difunctional (two oxirane rings per resin molecule), so the number of cross-links per resin molecule was theoretically equivalent given that a constant molar ratio of cross-linking agent, the amine hardener, was used in each case. The cross-link density, however, was variable due to differing separation (resin chain length) between cross-link points (oxirane rings, Figure 1). Furthermore, the siloxane, aliphatic, and aromatic chains possess very dissimilar flexibility.[40] Consequently, the rigidity of the various matrices studied should differ greatly, and it is thus not surprising that holographic performance failed to track merely with refractive index of the matrix. Of the low-index matrices prepared, one can predict on the basis of theoretical cross-link density and chain flexibility an order of matrix rigidity as EPS1 ≪ BDGE < DEO,[49] which correlates with the observed holographic performance of these materials.

Considering the importance of matrix rigidity to holographic performance, an effort was made to adjust the cross-link density and thereby optimize the performance of the BDGE/DTA materials. This was accomplished by varying the amine hardener (DTA) to epoxy resin ratio. DTA possesses five active amine protons that can open an oxirane ring, so considerable latitude in the extent of cross-linking was possible. The highest cross-link density was anticipated for a 1:1 ratio of N−H to oxirane (Figure 1). At a ratio of 2.5:1 the cross-linking was expected to be very low, as theoretically this ratio could yield linear polymers possessing no cross-links. Figure 7 shows the dependence of dynamic range on N−H:oxirane ratio of BDGE/DTA.

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(49) Note that this has not been corroborated through mechanical properties testing, but qualitative inspection is consistent with the predicted order of rigidity.
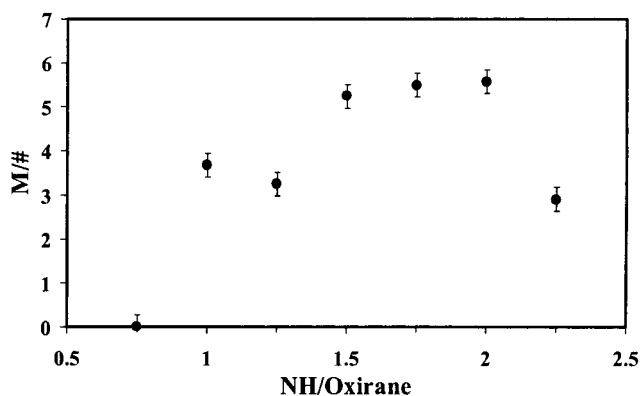
Figure 7. M/# as a function of amine hardener (DTA) to epoxy resin (BDGE) ratio. The data are presented as reactive functional group ratio rather than molecular ratio. All formulations contained 15% (v/v) NVC/NVP (50/50) photopolymer mixture and were scaled to constant total volume. M/#'s were normalized to the mean sample thickness of 0.294 mm (note that sample spacers do not give uniformly reproducible thickness, hence the need for normalization).
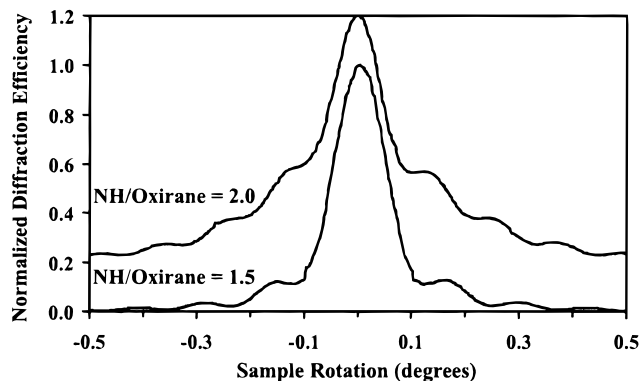
Figure 8. Angular response curves for 0° holograms in 0.5 mm thick samples of BDGE/DTA having N−H:oxirane ratios of 1.5 and 2.0. The samples contained 15% (v/v) NVC/NVP (50/50). The diffraction efficiencies were normalized to 1. The reduced distortion in the lower amine sample was presumably due to either increased resistance to shrinkage, or reduced polymerization due to the increased rigidity of the matrix as compared to higher amine containing materials.

Maximum performance was obtained for a ratio of 1.5−2:1, which corresponds to a modest degree of cross-linking. Performance dropped off dramatically above and below this range. Below 1.5:1, the matrix was presumably very rigid. A rigid matrix can potentially inhibit monomer diffusion and thereby prevent all of the photopolymer from being used during hologram encoding.[43] Further, optimization of the index contrast likely requires the matrix to be flexible enough to be pushed out of the irradiated areas of the material as photopolymerization occurs. Above 2:1, performance may have diminished because the matrix became too flexible. Some cross-linking is likely necessary to lock encoded holograms in place. Indeed previous experiments on entirely photopolymeric systems have shown that the best results are obtained when an oligomer is included to impart some cross-linking.[43]

We expected that moderate cross-linking would yield optimal performance, therefore a 2:1 ratio of N−H to oxirane was generally implemented in this study. Significant advantages were observed, however, by reducing the ratio to 1.5:1. Figure 8 compares holograms

recorded in 0.5 mm thick samples containing 15 vol % NVC/NVP. Distortion was dramatically reduced in the 1.5:1 matrix compared to the 2:1 matrix, possibly because the more rigid matrix in the former resisted shrinkage. A reduction in nonuniform shrinkage and consequent distortion due to enhanced mechanical properties has previously been demonstrated.[50] Adjusting matrix composition, then, may enable thicker samples exhibiting higher capacities to be prepared. In Figure 9, the temporal stability of encoded holograms (not to be confused with preexposure aging illustrated by Figure 5) is compared. For the 2:1 matrix, an ~24% reduction in M/# was observed over 25 days and considerable distortion developed. With the 1.5:1 matrix, M/# reduction was only ~10% and very little distortion developed. Both of these samples were stable after 25 days. The nature of the initial instability is unclear, but with a suitable matrix it appears that much of the deterioration can be eliminated.

Conclusion

The strategy of embedding photopolymers in an epoxy matrix offers a promising direction for holographic data storage materials. Thick samples (several millimeters) can be easily prepared, allowing for high data storage capacity. M/# values up to 13 have been achieved, and much better performance is anticipated if shrinkage-related distortion can be eliminated. Ample opportunities exist for reducing distortion and optimizing epoxy-based holographic materials. A large selection of epoxies, amines, and photopolymers are available that will allow adjustment of refractive index, mechanical properties, and shrinkage. Furthermore, within any given material system, composition, and therefore performance, can be varied over a wide range. Perhaps the greatest technical hurdle for developing these materials lies in the improvement of long-term, post-write thermal stability.

(50) Weiss, V.; Friesem, A. A.; Millul, E. *Proc. SPIE* **1996**, *2851*, 110.
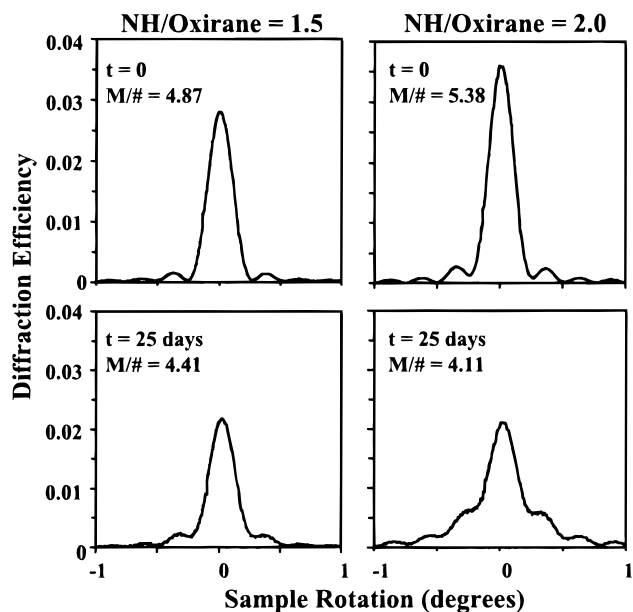
Figure 9. Un-normalized angular response curves (0° holograms) for 0.25 mm thick samples of two different BDGE/DTA matrices, each containing 15% (v/v) NVC/NVP (50/50): (Left) N−H:oxirane = 1.5; (right) N−H:oxirane = 2. For each material, curves obtained immediately after the holograms were written (top) and after 25 days of sample storage at room temperature (bottom) are represented. The sample with higher amine content exhibited greater loss in diffraction efficiency and much greater distortion with time than its lower amine counterpart.

Although concerted efforts have not yet been undertaken to address this issue, possibilities for improvement have already been observed through variation of the epoxy-to-hardener ratio of the matrix.