VOL. 9, NO. 1 JANUARY 1998

SPIE's International Technical Group Newsletter

Holography

HOLOGRAPHYONLINE

info-holo@spie.org

Here's an easy way to reach your colleagues around the world—instantly. SPIE's **Holography Listserv** is an automated e-mail server that connects you to a network of engineers, scientists, vendors, entrepreneurs, and service providers.

SPIE's Holography Listserv has its roots in the well-established and active Holography Technical Group, and is yet another way to use SPIE's technical resources.

To join the Holography Listserv, send an e-mail message to `info-holo-request@spie.org` with the words `subscribe info-holo` in the message body.

For detailed instructions, as well as information about other online SPIE services, such as Abstracts Online, Employment Services, and Technical Programs Online, send a message to `info-spie-request@spie.org` with the word `help` in the message body.

SPIE The International Society for Optical Engineering

Holography

This newsletter is published semi-annually by SPIE—The International Society for Optical Engineering for its International Technical Group on Holography.

Technical Group Chair	Michael Klug	*Managing Editor*	Linda DeLano
Technical Editor	Sunny Bains	*Advertising Sales*	Roy Overstreet

SPIE is an international technical society dedicated to advancing engineering, scientific, and commercial applications of optical, photonic, imaging, electronic, and optoelectronic technologies. Its members are engineers, scientists, and users interested in the development and reduction to practice of these technologies. SPIE provides the means for communicating new developments and applications information to the engineering, scientific, and user communities through its publications, symposia, education programs, and online electronic information services.

SPIE—The International Society for Optical Engineering, P.O. Box 10, Bellingham, WA 98227-0010 USA. Phone: (1) 360/676-3290. Fax: (1) 360/647-1445.

European Office: Contact SPIE International Headquarters.

In Japan: c/o O.T.O. Research Corp., Takeuchi Bldg. 1-34-12 Takatanobaba, Shinjuku-ku, Tokyo 160, Japan. Phone: (81 3) 3208-7821. Fax: (81 3) 3200-2889. E-mail: otoresco@gol.com

In Russia/FSU: 12, Mokhovaja str., 121019, Moscow, Russia. Phone/Fax: (095) 202-1079. E-mail: edmund@spierus.msk.su.

Want it published? Submit work, information, or announcements for publication in future issues of this newsletter to Sunny Bains at sunny@spie.org or at the address above. Full submissions guidelines are available at http://www.sunnybains.com/newslet.html. All materials are subject to approval and may be edited. Please include the name and e-mail address of someone who can answer technical questions. Calendar listings should be sent at least eight months prior to the event.

Polymers as holographic recording materials

The work of our research group has been mainly centered on the development, analysis and optimization of holographic recording materials like photographic emulsions, silver-halide, sensitized gelatin, and polymers. In this paper, we will review our most recent research in polymers. Photopolymerizable materials for holographic recording is the goal of our research. A typical photopolymerizable system consists of a monomer—or mixture of monomers—in a polymer matrix, and a photoinitiator system composed of a dye and an electron-donor. These systems can be used in a cavity between two glass substrates (liquid compositions), or cast on a substrate as dry films. Our group has studied different compositions of photopolymerizable systems in both these formats and examined their characteristics.

Photopolymerizable liquid compositions

Solubility is one of the factors that determines the formulation of a liquid composition, where the viscosity grade of the composite is determined by the monomers used in the mixture. A formulation is optimized in two different ways. First, dyes or sensitizers are chosen so that the absorption peak of the material corresponds to that emitted by the design laser. Wavelengths near to 514 nm have been sensitized using xanthene dyes and newly-designed photoinitiators synthesized. Second, the concentration of monomers can be optimized, along with their ability to form polymers with the best optical properties, and the conversion necessary to produce the required index modulation.

In all experiments with these compositions, exposure was carried out using two collimated beams, each of which had the same incident intensity on the sample. The photopolymerizable mixture was placed between two glass substrates with 45-µm-thick spacers, and the diffraction efficiency was measured using an electronic shutter.

In our laboratory, the first liquid system was composed of a mixture of hydroxyethylmethacrylate (HEMA) and ethylenglicoldimethacrylate (EGDMA) in a volume ratio of 1:1. As sensitizers, 4,5-diiodosuccinylfluorescein and N,N-dimethylaniline (coinitiator) were used, their relationship optimized by the photocalorimetric method. The result was 500 mJ/cm^2 energy sensitivity and 30% diffraction efficiency.[1] Later, we combined two dyes (methylene blue and bengal rose) obtaining better results by reducing the inhibition time caused by oxygen dissolved in the material.

The second liquid system was obtained by using a similar mixture of monomers but modifying the photoinitiator. A combination of eosine and an amine with an alpha-oxooxime group produced an increase in the rate of polymerization, which improves when the group is attached covalently. One improvement related to commercial dyes and their mixtures is that our group has combined of two chromophores in the same molecule, which should mean that the material is panchromatic.[2] The best results have been obtained when trifunctional monomers such as pentaeritritholtriacrylate (PETA) have been used,[3] giving us diffraction efficiencies of 40% with an energy sensitivity of 800 mJ/cm^2.

Photopolymerizable Dry Films

Polyvinylalcohol is, in all cases, the polymer matrix used to coat the film onto glass. The photopolymerizable dry film is made when a photosensitive solution, composed of monomers and a photoinitiator system in PVA, is coated and dried at normal conditions for 20 hours. We have used different monomeric compositions in order to obtain high diffraction efficiencies with low exposure energies.

Experimental

We have obtained the optimal composition for a system composed of acrylamide, methylene blue and triethanolamine in a PVA film.[4] Sensitivities of 45 mJ/cm^2 and diffraction efficiencies of 80% have been obtained in 35-µm films when a grating with spatial frequency 1000 lines/mm is recorded at the Bragg angle using a He-Ne laser tuned at 633 nm, and then read out in real time with a He-Cd laser (441 nm). This material has been shown to be very stable: good results have been obtained using materials fabricated four months before.

A great improvement in the energy sensitivity of the material was obtained when a bifunctional monomer was added to the last system. In this case the material is composed of the monomers acrylamide and *N,N'*-methylenbisacryla-mide, sensitized with triethanolamine, photoinitiated by methylene blue, with all the components supported in dry polyvinylalcohol. The diffraction efficiency and the sensitivity were 80% and 15 mJ/cm^2, respectively, when recording gratings using the experimental setup described before.

The drawback of this system is the generation of noise gratings.[5] Using transmittance curves, we have studied the effect of aging by showing the formation of dispersive centers over the surface of the film caused by the precipitation of *N,N'*-methylenbisacrylamide.

In order to improve energetic sensitivities, and to increase the signal/noise ratio, we are using different mixtures of monomers. For example, *N,N'*-methylenbisacrylamide has been replaced by

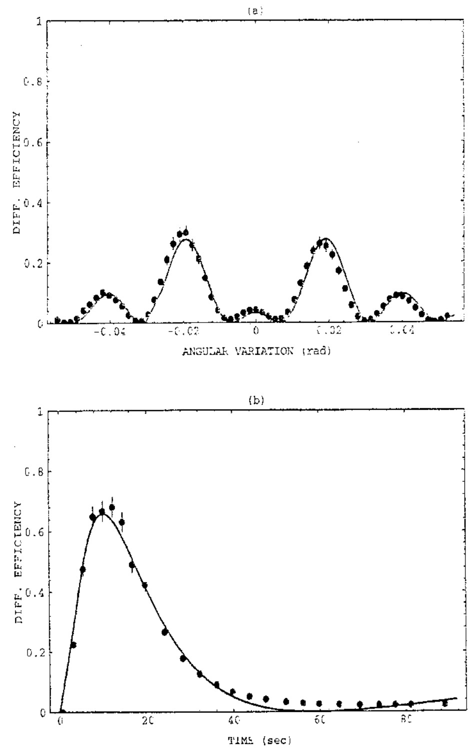

Figure 1. (a) Fitted curves of the angular response of diffraction efficiency and the corresponding experimental data. (b) Fitted curves of the growth in diffraction efficiency when thickness is 36-µm. Closed symbols are the experimental data and the curves are theoretically fitted, all of them being normalized to unity.

dihidroxyetilenbiscrylamide (DHEBA) and by HEMA. These systems have never been used as holographic recording materials.

To obtain sensitive materials in a broad range of the visible spectrum, the dyes used have been changed using xanthenes and other phenothiazines. A panchromatic system has been obtained, with great results, when a mixture of dyes of the families cited above have been used.

Theoretical

In these materials, the hologram is produced when bright zones in the polymerization process produce a polymer. The difference in refractive index between monomer and the formed polymer give the index modulation. A photo-polymerization process is produced when a photon is absorbed by the dye molecule, which by reduction reactions produce the Leucodye and radicals that initiate the polymerization reaction. We have developed a theoretical model[6] in order to use holography as a technique to analyze photo-polymerization processes: obtaining chemical parameters like polymerization constants and quantum yields. In this model, we used Kogelnik's theory to obtain an expression of the index modulation from a possible mechanism of polymerization, assuming that radical termination is produced and no diffusion processes occur during the polymerization reaction. We used transmittance curves to obtain the quantum yield of the bleaching process.[7] The polymerization constants were obtained by fitting all the experimental data of the angular responses and the temporal variation of the diffraction efficiency. Figure 1 shows the fitted curves of a material composed by acrylamide, triethanolamine, and methylene blue in a 35-μm thick PVA matrix.

Previously a theoretical model[8] was developed for materials where the process of polymerization was a copolymerization reaction. This model did not consider the details of this mechanism, assuming the simplest process of monomers to produce a copolymer.

L Carretero[1], S Blaya[3], R Mallavia[3], A Fimia[3], F Mateos[3], C Garcìa[1], M T Garzûn[3], I Pascual[1], R F Madrigal[3], A Belèndez[2], R Sastre[4], F Amat-Aguerri[4]

1. Laboratorio de Optica. Departamento Interuniversitario de Optica. Universidad de Alicante, Apdo. 99, Alicante 03080, Spain. E-mail: luis@aclis.labopti.ua.es
2. Departamento de Fìsica, Ingenierìa de Sistemas y Teoría de la seòal. Universidad de Alicante, Apdo. 99, Alicante 03080, Spain.
3. Departamento de Ciencia y Tecnologìa. Universidad Miguel Hernandez. Paseo Melchor Botella s/n, Apdo. 03206, Elx (Alicante), Spain.
4. Instituto de Quìmica Organica e Instituto de Ciencia y Tecnologìa de Polìmeros, C.S.I.C., Juan de la Cierva 3, E-28006 Madrid, Spain.

References

1. A Fimia, N Lopèz, F Mateos, R Sastre, J Pineda, and F Amat-Guerri, *New photopolymer used as a holographic recording material*, **Appl. Opt. 32**, p 3706, 1993.
2. R Mallavia, F Amat-Guerri, R Sastre, and A Fimia, *Synthesis and evaluation as visible-light polymerization photoinitiator of a new eosin ester with an o-benzoyl-alpha-oxooxime group*, **Macromolecules 27**, p 2643, 1994.
3. R Mallavia, A Fimia, L Carretero, S Blaya, F Amat-Guerri, and R Sastre, *Photopolymer recording material: optimization process with o-benzoyl-alpha-oxooxime and pentaerytritol triacrylate*, Submitted to **Applied Physics B.**
4. S Blaya, L Carretero, R Mallavia, A Fimia, M Ulibarrena, and D Levy, *Optimization of an acrylamide-based dry film used for holographic applications*, Submitted to **Applied Optics.**
5. L Carretero, S Blaya, A Fimia, A Belèndez, and R Madrigal, *Real time transmittance function in photopolymers of acrylamide composition: noise gratings*, **Proc. SPIE 2951**, pp 20-24, 1996.
6. S Blaya, L Carretero, R Mallavia, and A Fimia, *Holography as a technique for the study of photopolymerization kinetics in dry polymeric films with a non-linear response*, Submitted to **J. Am. Chem. Soc.**
7. L Carretero, S Blaya, R Mallavia, R F Madrigal, A Belèndez, and A Fimia, *Theoretical and experimental study of the bleaching of a dye in a film polymerization process*, Submitted to **Applied Optics.**
8. A Fimia, L Carretero, A Beléndez, *Nonlinear response of photopolymers for holography copolymerization process*. **J. Mod. Opt. 42**, pp 1351-1354, 1995.