Self-Processing, Diffusion-Based Photopolymers for Holographic Applications

Marc-Stephan Weiser,[*1] *Friedrich-Karl Bruder,*[2] *Thomas Fäcke,*[1] *Dennis Hönel,*[1] *David Jurbergs,*[3] *Thomas Rölle*[1]

Summary: The new photopolymers for holographic applications described herein are based on a cross-linked matrix in which the holographic grating is formed by photo-polymerization of guest monomers in an interference pattern of the recording light. Diffusion of monomer, triggered by this photo-polymerization, from the dark to the bright fringes of the interference pattern is the key parameter for creating high modulation in refractive index Δn during hologram recording. This leads to bright visual volume holograms with high diffraction efficiency. The holographic photo-polymers are self-processing. After recording the hologram only (incoherent) light exposure is necessary to bleach the final product and fix the hologram. Unlike earlier photopolymers used in holography, these new materials offer the advantages of no chemical or thermal processing combined with low shrinkage and detuning. Additionally, due to good light sensitivity the formation of the holograms is fast and the film obtained after curing is highly transparent, which makes the material suitable for both, reflection and transmission holography.

Keywords: diffusion; full color volume holograms; holography; photo-polymerization; self-processing

Introduction

Early holographic materials required cumbersome wet-chemical processing to develop the hologram after laser exposure.[1,2] For this reason, there has long been the desire to have an ideal volume holographic material that offers easy processing, long-term stability, accuracy of grating reproduction and compatibility to standard industrial product-integration processes.

The introduction of the first generation of holographic photopolymers to the industry in the late 1980's marked the beginning of a new era of volume holography.[3-5] Despite their advantageous properties, these materials made only limited inroads to commercial holographic applications. One reason for this was the fact that these materials still require some wet or thermal post-processing after hologram exposure. Additionally, they show rather low sensitivity in the longer wavelength spectrum above 600 nm.

This paper reports a new class of full color recording materials for volume holographic applications suitable to meet commercial manufacturing needs. There are diverse opportunities for holography, yet many of these have not been achieved on an industrial scale.[6]

The new photopolymers for holographic applications described herein are based on a cross-linked host matrix in which the holographic grating is formed by photo-polymerization of guest monomers. Diffusion of monomer from the dark to the

[1] Bayer MaterialScience AG, BMS-CAS-FF-R&D-CCH, D-51368 Leverkusen, Germany
Fax: (+49)-214-3096-43168;
E-mail: marc-stephan.weiser@bayerbms.com
[2] Bayer MaterialScience AG, BMS-PCS-GI-PHY-ODS, D-47812 Krefeld, Germany
[3] Bayer MaterialScience LLC, BMS-CAS-MKT-FF-KAM, Austin, TX-78708-1218, USA

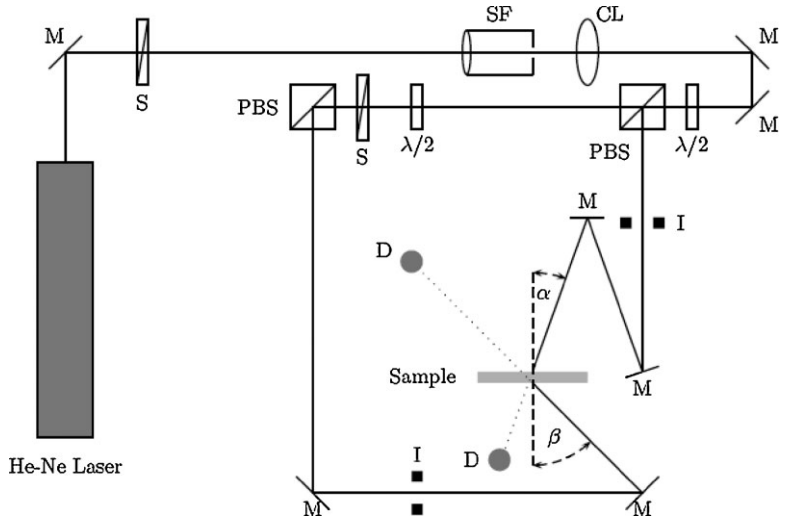

Figure 1.
M = Mirror, S = Shutter, SF = Spatial Filter, CL = Collimation Lens, λ/2 = Half Wave Plate, PBS = Polarizing Beam Splitter, D = Detector, I = Iris, α= 21.8°, β = 41.8°, wavelength of the He-Ne laser = 633 nm (similar testers for other wavelengths are available with similar set-up).

bright fringes of the recording interference pattern of the two laser beams is the key parameter for creating high modulation in refractive index during hologram recording if the index of refraction of the host matrix and the guest monomer are different. This leads to bright visual volume holograms with high diffraction efficiency. The holographic photopolymers are self- processing. After recording the hologram only (incoherent) light exposure is necessary to bleach the final product.

Method

For the preparation of the holographic media samples, matrix precursors and imaging components are dissolved, mixed and, if necessary, degassed at temperatures up to 60 °C. Typical chemical compositions have been reported elsewhere.[7] Glass beads are used as spacers to achieve the desired photopolymer thickness. The preparation is carried out under suitable light conditions. The resin is applied between the two glass plates and the formulation is hardened at room temperature for the formation of the cross-linked matrix. Film samples in which the resin is applied on a transparent substrate film such as polycarbonate or PET are laminated to a glass plate for holographic testing with the photopolymer side facing the glass surface. The holographic performance is examined using a Holographic Media Tester (Figure 1).

The holographic performance of the photopolymer formulations is measured in a plane wave tester as depicted above at a suitable laser wavelength. The photopolymers described herein are sensitive for red, green and blue light of most of the industrial viable laser wavelengths. Experimental data was collected at recording wavelength of 633 nm (red) or 532 nm (green), respectively. The holograms were recorded in reflection geometry. The diameter of each beam was collimated to be 4 mm. The power of the reference beam was set to 0.50 mW and the power of the signal beam was set to 0.65 mW to account for the different inclination angles of the two beams on the sample surface.

Figure 2 shows Bragg curves for holograms recorded in photopolymer at 633 nm

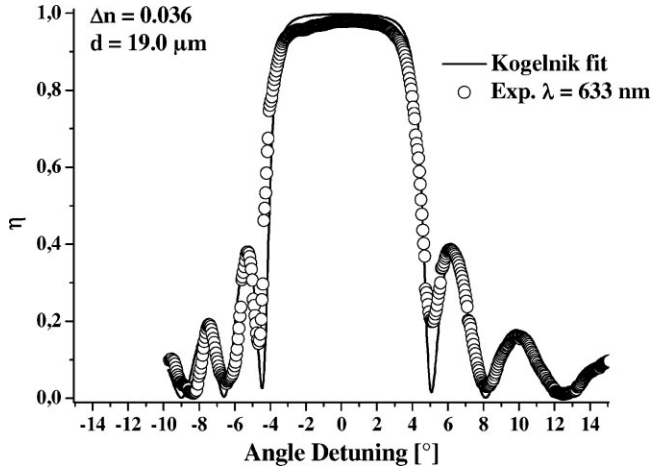

Figure 2.
Bragg-curve of 19 μm thick photopolymer film sample on PET 36 μm substrate laminated to glass measured using a laser wavelength of 633 nm.

wavelength along with curve fits to Kogelnik's model.[8] As can be seen from this figure, the experimental data closely matches the Kogelnik model, indicating that there is a very high optical quality from these materials. The refractive index modulation Δn of the grating and the thickness d of the photopolymer can be extracted from this model fit to the experimental data.

Working Principle of Bayer Photopolymer

Photopolymers are preferred recording materials for holograms, especially when offering the advantage of being self-developing systems. The recording step in these photopolymers requires the interaction of a photo-initiating system in the presence of light with a guest monomer to start photopolymerization within the bright fringes of the interference pattern. Normally the photosensitive compounds and guest monomers are dissolved in a host cross-linked matrix or a binder. Therefore, one of the key components of the photosensitive material used in photopolymers is the photo-initiating system, responsible for the photo-polymerization efficiency. The photo-polymerization efficiency is determined by different parameters such as the molecular absorption coefficient at the wavelength of recording light, quantum yield of radical formation, reactivity of photoproducts, and the possibility of photo-bleaching during or after photo-polymerization. All of these parameters have to be well balanced in order to obtain the maximum conversion of the writing chemistry in the bulk of the photopolymer material.[9]

During recording the hologram the sample is exposed to an interference pattern of light, containing bright and dark fringes, which is indicated by bright stripes in Image 1, Figure 3. Within the bright fringes, a sensitizer reacts with the light creating radicals to start the photo-polymerization of the so-called writing monomer (Image 2, Figure 3). Due to the consumption of monomer (Image 3, Figure 3), a concentration gradient is induced within the photopolymer layer, resulting in diffusion of monomer from the dark to the bright fringes (Image 4, Figure 3).[10] This leads to a mass transfer within the photopolymer and an accumulation of polymerized writing monomer within the bright fringes and low concentration of monomer with remaining matrix in the dark fringes. This diffusion controlled process is the key parameter for high monomer conversion within the bright

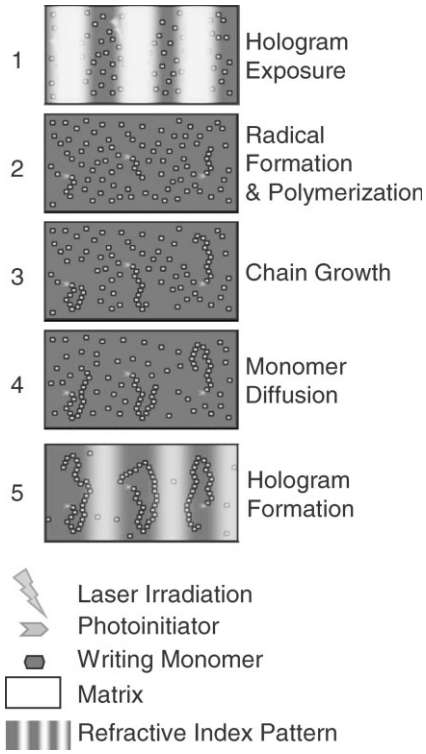

Figure 3.
Working principle of Bayer photopolymer.

fringes and a formation of high refractive index modulated holographic grating. Thus, the interference pattern of the light is recorded within the photopolymer by a chemical modification inside the film (Image 5, Figure 3).

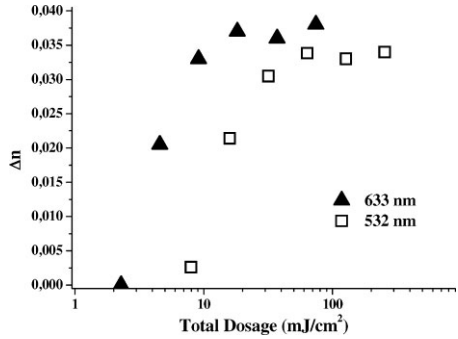

Figure 5.
Build-up curves for Bayer photopolymer film samples recorded at 633 nm and 532 nm laser wavelength.

Results and Discussion

The compositional grating formed within the photopolymer during holographic exposure can be made visible by transmission electron microscopy as shown in Figure 4. The observed grating period Λ in this example is 550 nm.

In Figure 5, growth curves for Bayer photopolymer film samples are shown for recording at both, 633 nm and 532 nm laser wavelength. For the red testing, Δn saturation is observed for a total dosage as low as 10 mJ/cm^2. For the green testing the dosage necessary to reach saturation of refractive index modulation is 30 mJ/cm^2.

These results demonstrate the ability that high refractive index modulations of $\Delta n > 0.035$ can be achieved in new Bayer

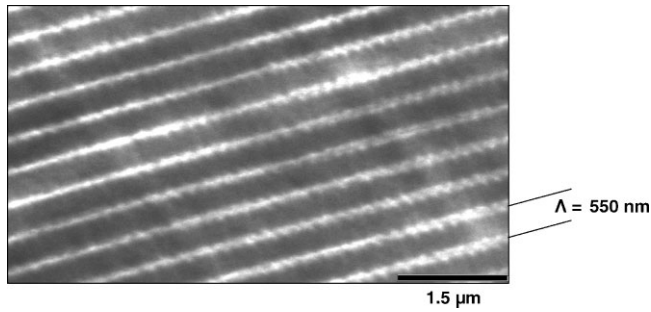

Figure 4.
TEM image of a compositional grating which forms the hologram with a grating period Λ of 550 nm. The bright areas represent the areas in which photo-polymerization and diffusion accumulated and polymerized the guest monomers.

photopolymers without the need for thermal post-processing. The above described diffusion mechanism can be controlled at ambient temperatures. These data also reveal the high photosensitivity for both, red and green recording of the new Bayer photopolymer. It is remarkable that high red sensitivity can be obtained although especially the low energy of red photons is expected to be an extra challenge from the thermodynamics point of view.[11]

While in this paper the experimental focus is set on 633 nm and 532 nm exposure, the material is also sensitive to other laser wavelengths of the visible light spectrum. Therefore, the material is suitable for recording full colour holograms at most of the available industrial laser wavelengths, e. g. such as 473 nm for blue recording.

Conclusion

A large number of potential commercial applications for volume holographic materials exist due to their unique properties to generate holographic gratings for numerous applications in the optical, security, display and advertising & branding industry. Here, we describe the development of a new class of full-color photopolymer materials that are well suited to address the unmet needs in the marketplace. The new photopolymers are suitable for recording both, reflection and transmission holograms, as well as edge-lit holograms. The holograms recorded in Bayer photopolymer are self-processing allowing the formation of the holographic grating without the need for thermal or chemical post-processing. Diffusion of writing monomers from the dark to the bright fringes during photo-polymerization induced by the holographic recording is the key parameter for the formation of the grating. The ease of handling, coupled with their strong holographic performance makes these photopolymers well suited to enable a broad commercial breakthrough of volume holography.

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