Full-Color Self-processing Holographic Photopolymers with High Sensitivity in Red - The First Class of Instant Holographic Photopolymers

Friedrich-Karl Bruder², François Deuber¹, Thomas Fäcke¹, Rainer Hagen¹, Dennis Hönel¹, David Jurbergs⁴, Masaro Kogure³, Thomas Rölle¹, and Marc-Stephan Weiser¹*

¹ Bayer MaterialScience AG, BMS-CAS-FF-HOL, D-51368 Leverkusen, Germany;
² Bayer MaterialScience AG, BMS-PCS-GI-PHY-ODS, D-47812 Krefeld, Germany;
³ Bayer MaterialScience Ltd., 1-6-3 Marunouchi, Chiyoda-ku, Tokyo, 100-8211 Japan; and
⁴ Bayer MaterialScience LLC, BMS-CAS-MKT-FF-KAM, Austin, TX-78708-1218, USA.

The new holographic photopolymers described herein are based on a cross-linked matrix in which the holographic grating is formed by photopolymerization of guest monomers in an interference pattern of the recording light. Diffusion of monomer, triggered by this photopolymerization, from the dark to the bright fringes of the interference pattern is the key parameter for creating high modulation in refractive index during hologram recording. 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 and fix the hologram. The full color photopolymers show exceptionally high sensitivity for red laser light (633 nm).

Keyword: holography, full color volume holograms, photopolymerization, sensitivity, self-processing, grating formation.

1. 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;4;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 holographic photopolymers described herein are based on a cross-linked host matrix in which the holographic grating is formed by photopolymerization of guest monomers. Diffusion of monomer from the
dark to the 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. The full color photopolymers show exceptionally high sensitivity for red wavelength spectrum. The required dosage for saturation of refractive index modulation at 633 nm is below 10 mJ/cm².

2. Results and Discussion

2.1 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. 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. The holographic performance is examined using a Holographic Media Tester (Figure 1).

Figure 2: Bragg-curve of glass coupon sample measured at 633 nm.

Figure 2 shows Bragg curves for holograms recorded in photopolymer at 633 nm wavelength along with curve fits to Kogelnik’s model [7]. 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 \( \Delta n \) of the grating and the thickness \( d \) of the photopolymer can be extracted from this model fit to the experimental data.

2.2 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 photoinitiating 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 wavelength of 633 nm. 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.
components of the photosensitive material used in photopolymers is the photoinitiating system, responsible for the photopolymerization efficiency. The photopolymerization 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 photobleaching during or after photopolymerization. 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 [8].

During recording the hologram the sample is exposed to an interference pattern of light, containing bright and dark fringes, which is indicated by yellow stripes in Image 1, Figure 3. Within the bright fringes, a sensitizer reacts with the light creating radicals which start the photopolymerization 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) [9]. 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. Thus, the interference pattern of the light is recorded within the photopolymer by a chemical modification inside the film (Image 5, Figure 3).

The compositional grating formed within the photopolymer during holographic exposure can be made visible by transmission electron microscopy as shown in Figure 4.

In Figure 5, build-up curves for Bayer photopolymer are shown for both, glass coupons and film samples, recorded at 633 nm laser wavelength. For the red testing, $\Delta n$ saturation is observed for a total dosage of only 10 mJ/cm$^2$. This reveals the high photosensitivity of new Bayer photopolymer.

![Figure 3. Working principle of Bayer photopolymer.](image1)

![Figure 4. TEM image of a compositional grating which forms the hologram with a grating period $\Lambda$ of 550 nm. The bright areas represent the areas in which photopolymerization and diffusion accumulated and polymerized the guest monomers.](image2)
These results demonstrate the ability that high refractive index modulations of $\Delta n > 0.03$ can be achieved in glass coupons as well as in film products without the need for thermal post-processing. The above described diffusion mechanism can be controlled at ambient temperatures. 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. While in this paper the experimental focus is set on 633 nm exposure, the material is also sensitive to other laser wavelengths of the visible light spectrum such as 476 nm and 532 nm.

Bayer Material Science plans to commercialize this new class of full-color film products under the tradename Bayfol® HX in 2010. First trial products with different performance will be available earlier. It is anticipated that future commercial products will exhibit holographic performances exceeding the values given above.

3. Conclusions

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. They do not require chemical or thermal processing, and show high transparency, high resolution, environmental stability and precision of gratings. The new photopolymers are suitable for recording both, reflection and transmission holograms, as well as edge-lit holograms. In this paper the remarkable high sensitivity in the red visible wavelength spectrum is demonstrated. The ease of handling, coupled with their strong holographic performance, makes these photopolymers well suited to enable a broad commercial breakthrough of volume holography.

References