



Recording and thermo developing of latent phase holograms in the photosensitive polymer material based on anthracylacetoneboron difluoride



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ARTICLE INFO

Article history:

Received 25 January 2015

Received in revised form 31 March 2015

Accepted 13 April 2015

Available online 8 May 2015

Keywords:

Photosensitive polymer

Anthracylacetoneboron difluoride

Laser modification

Latent recording

Diffusion development

ABSTRACT

The diffraction efficiency of photoinduced gratings recorded in polymethylmethacrylate doped with anthracylacetoneboron difluoride was shown to be increased from 8% to 70% due to the post-exposure heating of the material to 75 °C. Mechanism of the thermal development was determined to be the diffusion of the initial photoactive additives molecules and the photoproduct. This process shifts the minimum of the material frequency-contrast characteristic into the low-frequency region as well as significantly increases the amplitude of the refractive index modulation for gratings with the spatial frequencies up to 2500 mm⁻¹.

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1. Introduction

Large number of photorecording materials are currently being developed for laser recording of the integrated diffractive optical elements (DOEs) widely used for transfer, conversion and processing of optical signal. Photosensitive polymer materials (PPMs) being compared with the classical recording media based on silver halides emulsions and dichromated gelatin layers have a number of advantages including their low cost, high adaptability and spatial resolution, low light scattering as well as phase photoregistration ability without the liquid photographic post-exposure, so these materials are currently of great interest [1–4]. However, the recording of the latent images remains the major advantage of conventional photorecording media being compared to the PPMs. Indeed, the tendency to the self-development of polymeric photomaterials at their exposure process leads to the distortion of the exposure radiation wavefront due to the diffraction processes in the developed structures as well as to the appearance of noises and poor quality of the recording DOEs, in turn [5–7]. The fabrication of the thick (at least 1-mm-thick) PPMs supporting the latent phase recording is complicated by time-consuming conventional liquid scheme of the postexposure development caused by the slow diffusion of chemical reagents of the polymer matrices [7]. The post-exposure

enhancement of the holograms based on the diffusion relaxation of the complementary gratings can be used to solve this problem [2,8,9]. In particular, the PPMs containing the anthracene and its derivatives exhibit this effect [10,11]. Such PPMs demonstrate the ability to record almost latent holograms, however, these materials are characterized by low stability of the chemical composition and structure at their utilization. In this regard, the developing of novel highly stable PPMs based on anthracene as well as studying their properties are of great interest.

Previously, we reported a fabrication of the polymer material based on polymethylmethacrylate (PMMA) doped with the novel additive, an anthracene – 2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine (AntBF₂). This polymer material can be efficiently used for laser recording of the thin and thick (thicker than ~1 mm) phase DOEs [12] as well as thin-film integrated optical elements [13]. Our experiments show that very weak, almost latent, phase images demonstrating the possibility of subsequent thermo development and sufficiently long (longer than one year) post-exposure storage without significant changes of their optical properties can be record in such material at sufficiently low exposures. In this paper, these capabilities of material are studied in detail.

2. Model of grating formation

The material under study is a solution of the photoactive AntBF₂ additives in methacrylate polymerized in block [12].

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Photochemical processes in this material are mostly limited to photodimerization of the additive molecules as in the case of AntBF₂ crystals [14]. Despite the fact that the nature of the photochemical processes in this material is not fully understood, in the framework of this paper we can conclude that the photoproduct molecules are larger than the molecules of the original photoactive additives and therefore have much lower mobility.

Let us consider the case of the sinusoidal grating recorded in this material. We assume that the recording occurs in the interference field of crossed coherent beams. The sample's material is assumed to be thin enough, thus the intensity of the exposure radiation is uniformly distributed along the sample depth. Thus, the change in the concentration of the original photoactive AntBF₂ molecules $C^{(1)}$ and their photoproduct $C^{(2)}$ occurring under the action of the exposing radiation will be described by a system of equations [15,16]

$$(-1)^m \gamma I(x) C^{(1)}(x, t) \Phi(t) + D_m \frac{\partial^2 C^{(m)}(x, t)}{\partial x^2} = \frac{\partial C^{(m)}(x, t)}{\partial t}, \quad m = 1, 2 \quad (1)$$

with the following initial conditions $C^{(1)}(x, 0) = C_0$, $C^{(2)}(x, 0) = 0$, where $I(x) = I_0[1 + \cos(2\pi x)/\Lambda]$, Λ and I_0 are the distribution, modulation period and the average intensity of the interference field, respectively; γ – constant characterizing the photochemical reaction rate, D_1 and D_2 – diffusion coefficients of the original photoactive additive and photoproduct in the PMMA matrix, respectively; $\Phi(t)$ is a step function, which is equal to 1 at $0 \leq t \leq t_0$, and zero – at all other cases, t_0 – the exposure duration. The first term of the left side of the system (1) is associated with the photodimerization, while the second one – with the diffusion arising from the molecule concentration gradients caused by the spatially inhomogeneous radiation exposure, in turn. We will further assume that the molecule concentration distribution has the same period (Λ) as the exposure intensity distribution. In this case, the solution of the system (1) can be found in the range from 0 to Λ . The boundary condition in this case is described by the absence of material flow through this boundary: $\frac{\partial C^{(m)}(x, t)}{\partial x} = 0$ [16]. Instead of finding the direct solutions of the system (1) we will look for the modulation amplitudes of $C^{(1)}$ and $C^{(2)}$ at a spatial frequency $\Omega = \Lambda^{-1}$, since these amplitudes eventually define efficiency of the first-order diffraction gratings.

Characteristic times of the grating diffusion modification are known to decrease with the growth of the spatial frequency Ω [10,17]. Therefore, there are quite low values of Ω , at which the characteristic time (τ_0) of grating diffusion modification will be much larger than the characteristic recording time (t_0). Therefore, when considering the formation mechanism of such gratings we can split by time the photochemical processes occurring at $t \leq t_0$, and diffusion processes – at $t > t_0$. At $t \leq t_0$ we can assume $D_1 = D_2 = 0$, hence the system (1) becomes the typical equation of photochemistry with the well-known exponential solution [18]. Expanding this solution in a Taylor series about the parameter $\gamma I_0 t$ one can find in a first approximation the first-harmonic amplitude of the concentration distribution of the original additives molecules and photoproduct.

$$-C_1^{(1)}(t) = C_1^{(2)}(t) \approx C_0 \gamma I_0 t e^{-\gamma I_0 t}. \quad (2)$$

Relation between $C_1^{(1)}$ and $C_1^{(2)}$ values and the first-harmonic amplitude of the refractive index (RI) distribution $|n_1|$ in the recorded grating is determined by Lorentz–Lorentz equation. Using this equation and assuming $|n_1| \ll n$ (n – material refractive index), one can obtain the following equation [10,19]:

$$n_1 = \frac{(n^2 + 1)^2}{6n} (C_1^{(2)} R_2 + C_1^{(1)} R_1), \quad (3)$$

where R_1 and R_2 are the molar refractions of the initial photoactive molecules and the photoproduct, respectively. It was experimentally

shown [12] that at uniform exposure the RI of the material under study decreases clearly indicating the negative value of n_1 . Note that this sign in Eq. (3) appears at $R_2 < R_1$. Negative value of the n_1 also points out the π -shift of the phase of the recorded RI grating relatively to the phase of the sinusoidally modulated interference field. Likewise, Eqs. (2) and (3) indicate that at $t_M = 1/\gamma I_0$ the RI amplitude $|n_1|$ reaches its maximum value $\approx 0.74|C_0(R_2 - R_1)|$. In accordance with Eqs. (2) and (3), further exposure decreases the $|n_1|$ value, which can be explained by the appearance of the high-order spatial harmonics contributing to the RI distribution.

After completion of exposure (at $t \geq t_0$) Eq. (1) transforms to the ordinary diffusion equation with the same boundary conditions, while at $\tau = t - t_0 = 0$ the initial conditions can be written in accordance with Eq. (2): $C^{(m)}(x, 0) = C_{av}^{(m)} + C_1^{(m)}(t_0) \cos(2\pi x/\Lambda)$, $m = 1, 2$, where $C_{av}^{(m)}$ is the average concentration, which has no effect on the amplitude $|n_1|$ of the recorded grating. The solution in this case can be written as

$$C_1^{(m)}(\tau) = C_1^{(m)}(t_0) e^{-\frac{\tau}{\tau_m}}, \quad (4)$$

where

$$\tau_m = \frac{\Lambda^2}{D_m(2\pi)^2}, \quad m = 1, 2. \quad (5)$$

If the abovementioned assumption on the reduction of the molecules mobility at their photomodification holds true, the diffusion coefficients of original additive molecules and the photoproduct will satisfy the inequality $D_1 > D_2$. In this case, the characteristic decay times of the amplitudes $C_1^{(1)}$ and $C_1^{(2)}$ in Eq. (4) will be different ($\tau_1 < \tau_2$). This means that the diffusion will lead to the decrease of the absolute value of the n_1 due to the faster relaxation of the $C_1^{(1)} R_1$ being compared with the $C_1^{(2)} R_2$. At characteristic time

$$\tau_0 = \frac{\ln(R_1/R_2)}{(D_1 - D_2)(2\pi\Omega)^2}, \quad (6)$$

when in accordance with Eq. (4) the following equality $C_1^{(1)} R_1 = -C_1^{(2)} R_2$ is satisfied, the amplitude $|n_1|$ becomes zero as can be seen from Eq. (3). At this point, the phase of the recorded grating is changed to π . Then, the absolute value of n_1 gradually increases reaching its maximum value at the time

$$\tau_M = \left(1 + \frac{\ln(D_1/D_2)}{\ln(R_1/R_2)}\right) \tau_0. \quad (7)$$

According to Eq. (3), the RI modulation amplitude of the grating in this case is $R_2/(R_1 - R_2)$ times higher than that of the end t_0 of the exposure process. This enchantment is the physical origin of the recorded grating development. From these considerations the role of material heating during the grating development becomes obvious [12]. Indeed, at room temperatures the diffusion coefficients D_1 and D_2 can be quite small and τ_M value will be high [20]. At the same time, moderate heating (few tens of Celsius degrees) of the exposed material leads to the significant increase of the diffusion coefficients, which causes the decrease of the grating development time to tens of hours [12], in turn. It should be noted that the grating cooling down to the room temperature immediately after reaching the maximum values of n_1 slows down the diffusion degradation process of the grating, with the characteristic time τ_2 of this process being determined by the diffusion coefficient D_2 of the photoproduct molecules in accordance with Eq. (5).

As it follows from Eq. (6), condition $\tau_0 \gg t_0$ holds true only for low-frequency gratings with the spatial frequency Ω , which is much smaller than the characteristic value

$$\Omega_0 = \sqrt{\frac{\ln(R_1/R_2)}{t_0(D_1 - D_2)(2\pi)^2}}. \quad (8)$$

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