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Peculiarities of the exposure of actinic radiation on polymeric holographic recording media

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Abstract. The results of experiments that allow to evaluate changes of optical parameters of polymeric recording medium with diffusional amplification occurring during recording of information are presented. It is shown that phase characteristics of the sample compared to its initial state are observed during recording of information and in the post-exposure period, i.e. in a stable condition of the finished element. Quantitative estimates which can be used for planning conditions of holographic experiment during creating highly selective holographic optical elements (HOE) with given parameters are obtained.

1. Introduction

Polymeric recording media with the thickness of the order of millimeter are used at the present time for scientific purposes and for the creation of highly selective holographic optical elements (HOE), for recording and archival storage of information. [1-3]. One of the most promising practically realizable materials for recording volume holograms are polymeric media with diffusion enhancement based on polymethyl methacrylate (PMMA) and phenanthrenequinone (PQ). Such materials are characterized by high resolution capability and information capacity of the samples in combination with available technology of their production. Their disadvantages include the fact that the change of physico-mechanical characteristics of polymer samples and their optical parameters during changing external conditions (including temperature and humidity) is significantly higher than other optical materials such as silicate glass or optical crystals.

Changes of parameters of the sample due to increase of its temperature should be taken into account when considering the recording process of the hologram, because the effect of actinic radiation (radiation with a wavelength in the spectral region of absorption of the sample) is accompanied by heating which leads to the change of the average refractive index and the thickness of the sample.

Thus, during recording of the hologram under the influence of the interferential field on the spatial-modulated changes of the optical characteristics of the sample (photoinduced changes) are superimposed spatial-unmodulated changes of its optical characteristics caused by heating.

If temperature changes of the refractive index of the sample are comparable with the amplitude of the photoinduced changes, this can lead to the fact that the spatial structure of recorded hologram will be different from the structure of the recorded interferential field. The accounting of such deformations, as well as optimization of the recording conditions to reduce thermal effects is particularly important in obtaining volume holograms designed for the creation of highly selective HOE. The available literature information about the effect of influence of temperature changes on parameters of recorded polymeric holograms is ambiguous, and often contradictory, as it refers to samples obtained in different conditions [1].

In this paper the spatial-temporal changes of phase characteristics of the polymer samples during action of actinic radiation, the presence of which may lead to deformation of recorded highly selective holographic structures, are considered and their quantitative evaluations are given.

2. Object and methods

Object of research: sample of material "Difphen" - one of the modifications of polymeric volume recording medium with diffusion enhancement based on PMMA/PQ [4]. On figure 1a are shown spectral characteristics of a typical sample of this material in the initial state (curve 1 – absorption spectrum due to the presence of PQ molecules in the sample of PMMA) and after complete bleaching of the sample (curve 2), when under the action of actinic radiation, there was a complete transformation of the light-sensitive molecules of PQ into not light-sensitive molecules of photoproduct (PP), which don't have absorption in the visible region of the spectrum.

For research of changes of optical characteristics of the sample in the process of radiation exposure and post-exposure period was used experimental stand designed for the research of phase transformations in transparent objects by method of digital holographic interferometry (DHI) [5], block-diagram of which is shown on figure 1b. On this stand an object node (3) placed outside the main scheme of the interferometer (1) which allows monitoring the process of external influence on the object by beam of radiation 473 nm DPSS-laser (4). The sample (disk with diameter 40 mm) is rigidly mounted in a special cassette and installed in the object beam in accordance with the optical scheme of interferometric experiment. The object beam of interferometer is a non-actinic test beam for this sample of radiation of 532 nm, which tests a workspace of the sample with the size not less than 25x25 mm. The beam of actinic radiation, extended by lens, passes through the sample in the center of workspace. This stand has a computer terminal to control registration of sequence of digital holograms and for their further processing.

The methodology of each experiment includes the following main stages [5]:
- recording of the sequence of digital holograms that show the current state of the sample during the experiment: before radiation exposure (the initial state), during the period of exposure (exposure) and in post-exposure period (relaxation);
- receiving a series of digital interferograms by processing sampling of recorded holograms;
- digital processing of interferograms and presentation of results in a convenient way.

The digital interferogram of the current state of the object represents by itself a spatial distribution of phase difference of the testing radiation in the plane of observation of object relevant to the change of the sample at the moment of time t_i compared to initial (at the moment of time t_0 before exposure) – $\varphi_{i0}(x,y) = \varphi_i(x,y) - \varphi_0(x,y)$. A typical view of interferogram of the sample status during the period of radiation exposure is shown in figure 1c. Interference pattern in this case takes the form of concentric rings with the center in the center of the exposure area. Outside of interference pattern ("pertubation" area of the sample) there is a uniform background. In further calculations it is assumed that in background area the phase difference between rays that have passed through the sample at time t_i and t_0 is equal to zero, i.e. $\varphi_{i0}(x,y)_{bg} = \varphi_i(x,y)_{bg} - \varphi_0(x,y) = 0$. Thus, $\varphi_i(x,y)_{bg} = \varphi_0(x,y)$ and the spatial distribution of the phase difference $\varphi_{i0}(x,y)$ will represent the value of $\varphi_i(x,y)$, measured from $\varphi_i(x,y)_{bg}$. The results of digital processing of interferogram is shown on figure 1d in the form of "detailed" phase difference along the x axis, $\varphi_{i0}(x)$, obtained by summing the phase incursions along the line A-A from background to the left from the center of exposure, where $\varphi_{i0} = 0$, through the center, where φ_{i0} is maximum, to the background right from the center; there are also the limits of beam of exposed radiation Δx_{exp} that gives an ability to compare their limits and the area of "phase perturbations" caused by this exposure.

By each current interferogram during processing were obtained the following quantitative data:
- change of the phase difference in the centre of exposure area $(\varphi_{i0})_c$ in the moment of time t_i;
- the sample area, Δx_{pert}, in which at the current time $\varphi_{i0} \neq 0$.

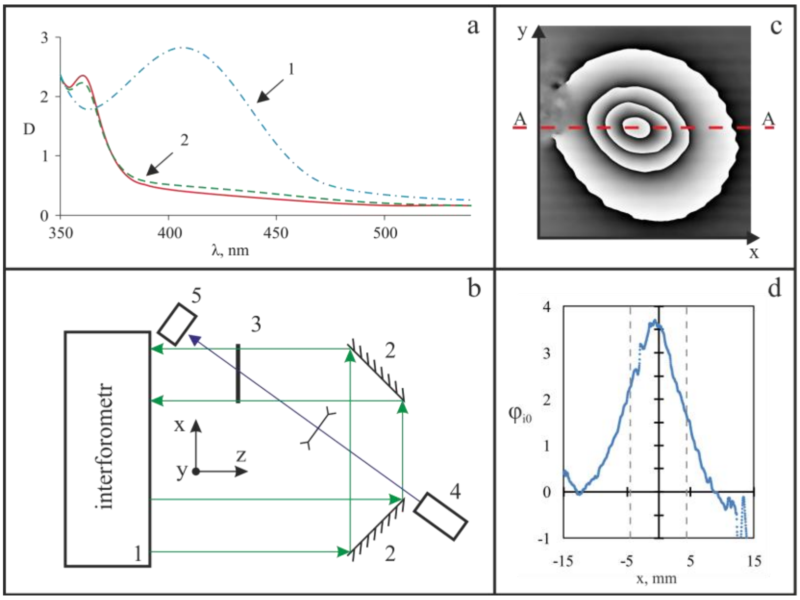

Figure 1. a – the spectral characteristics of sample of material "Difphen" before radiation exposure (curve 1) and after complete cycle of processing (curves 2); b – the block-diagram of the stand for experiments: 1 – interferometer, 2 – mirrors, 3 – object, 4 – laser 473 nm, 5 - detector; c – digital interferogram that shows the phase change of the test radiation (532 nm) during actinic radiation exposure (473 nm), d – detailed distribution of the phase difference, $\varphi_{i0}(x)$, along the line A-A and the limits of beam of exposed radiation Δx_{exp} (dashed lines).

3. Experimental results and analysis

The results of experimental data processing are presented on figure 2 and figure 3 for two sequences, in each of them holograms were recorded with an interval of one second and with 1/1024 s exposure: during exposure of radiation of 473 nm - during 10 minutes and after its ending – during 5 minutes. The power of radiation beam of 473 nm in experiment 1 was 20 mW, in experiment 2 it was 36 mW.

On figure 2 results of processing of mostly typical holograms are presented in the form of detailed distribution of phase difference on x-axis, $\varphi_{i0}(x)$, (centre of radiation exposure of 473 nm is located at x = 0). In both experiments during the period of radiation exposure $\varphi_{i0}(x) \geq 0$, and "perturbed" area considerably exceeds the area of exposure, i.e. $\Delta x_{pert} > \Delta x_{exp}$. In stable post-exposure condition of sample $\varphi_{i0}(x) \leq 0$ и $\Delta x_{pert} \approx \Delta x_{exp}$. This situation can be explained by the fact that the phase changes of the sample, that are diagnosed in the post-exposure period, due to photochemical transformations (conversion of PQ to PP), that occurred in the exposed area of the sample (Δx_{exp}) during the influence of actinic radiation. At the same time, the phase changes of the sample at the stage of exposure radiation is caused by two processes: phototransformation of PQ and heating of the sample. In the post-exposure period heating of the sample is not presented, and the fact that $\Delta x_{pert} \approx \Delta x_{exp}$ also suggests that in this case, the change of phase, $\varphi_{i0}(x)$, is determined only by phototransformation of PQ.

Exactly this process provides recording of information in given recording medium. Phototransformation of PQ leads to the change of the refractive index of the medium (Δn_{PQ}) ,thus, it is assumed that spatial changes of polymeric framework in this process are not happening - $\Delta l_{PQ} = 0$. The process of transformation of PQ into PP in the experiments is monitored by measuring the transmittance of the sample, τ, at 473 nm (curve 3, figure 3a). During full transformation of PQ transmittance of the sample reaches maximum value which doesn't change in the future. In the experiments it happens during first 200 seconds of exposure of the sample. Thus, $\Delta n_{PQ}(t_i) \approx$ const at t_i

> 200 seconds and change $\varphi_{i0}(t_i)$ is only due to heating by absorption of radiation energy. Heating of the sample leads to change of its refractive index and to change of its geometric dimensions and temperature changes of optical thickness of the sample $\Delta(nl)_{term}$ in this case determined by the properties of the polymeric framework and specific modification of the polymer.

Dependences 1 and 2 on figure 3a characterize phase changes of the sample $\varphi_{i0}(t_i)$ during radiation expose of 20 mW (1) and 36 mW (2). In the period of exposure the value $\varphi_{i0}(t_i)$ becomes higher after power increase; while during relaxation the difference between values $\varphi_{i0}(t_i)$ in experiments 1 and 2 are within the measurement error. The difference of values $\Delta x(t_i)$ (figure 3b) in both experiments is also within measurement error.

The obtained experimental results allow us making the following assessments:
- Changes of the sample during the period of exposure of actinic radiation include irreversible changes due to phototransformation of PQ, $\{\varphi_{i0}(x,y)\}_{PQ}$, and reversible due to heating $\{\varphi_{i0}(x,y)\}_{term}$.
- During exposure of radiation of $200 < t_i < 600$ seconds phase characteristics of the sample don't change significantly. During this period irreversible changes of the sample that determine the process of information recording, with the full phototransformation of PQ make the quantity of $\{\varphi_{i0}(x,y)\}_{PQ} = -(1{,}0\pm0{,}1)\pi$ rad, and reversible changes of the sample due to the heating make the quantity of $\{\varphi_{i0}(x,y)\}_{term} = \{\varphi_{i0}(x,y)\} - \{\varphi_{i0}(x,y)\}_{PQ}$, equal to $\approx 3\pi$ rad for experiment 1, which significantly exceeds the quantity of the irreversible changes which determine information recording.

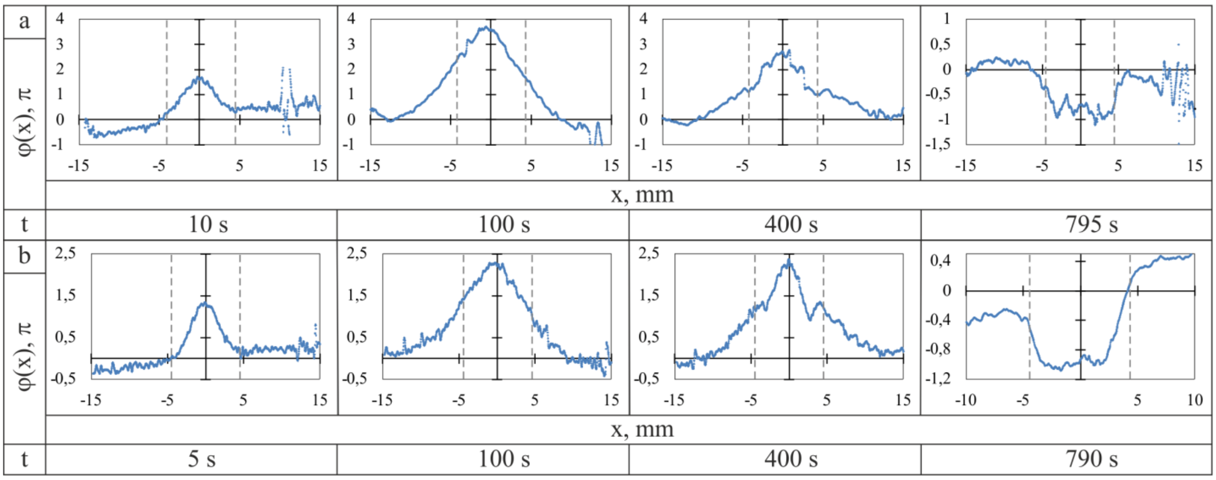

Figure 2. The change of phase $\varphi_{i0}(x)$ along the line A-A in experiments 1 (a) and 2 (b) - exposure of radiation of 473 nm in the period from 0 to 600 s. Vertical dashed lines determine Δx_{exp}.

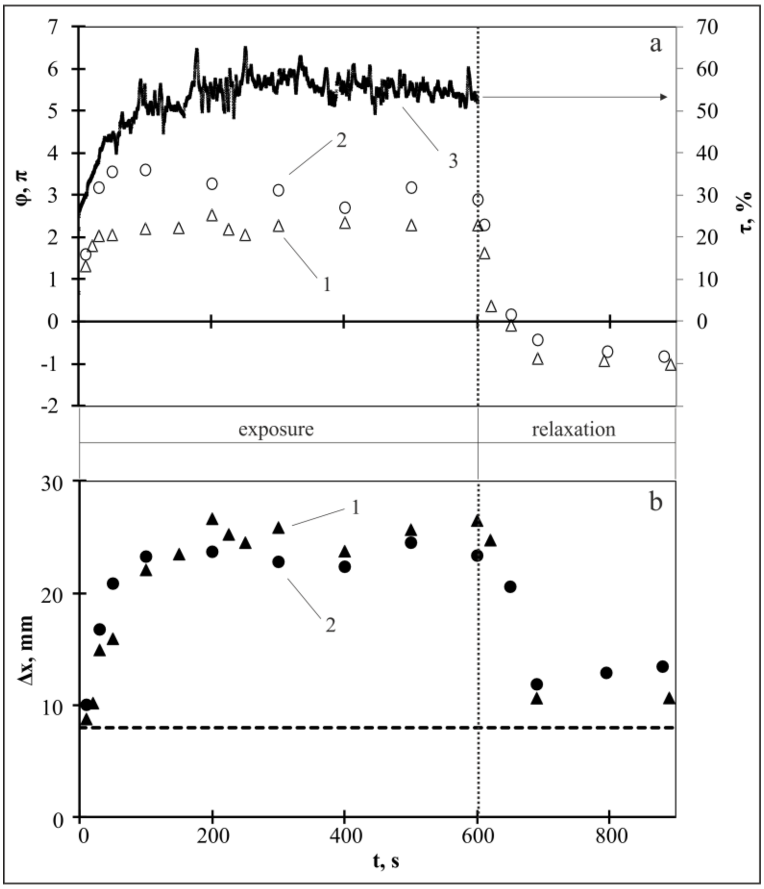

Figure 3. Dynamics of change of characteristics of polymeric sample during exposure of actinic radiation of 473 nm (exposure) and in post-exposure period (relaxation): a - phase change of testing radiation, φ_{i0}, in the center of the area of exposure of actinic radiation with power of 20 mW (experiment 1) and 36 mW (experiment 2, change of transmittance of the sample, τ, at wavelength of 473 nm (curve 3); b – change of the value of "phase perturbation" area (Δx_{pert}) in experiments 1 and 2; dashed line is the exposed sample area, Δx_{exp}.

4. Conclusions

The experiments with the use of the method developed by authors allowed quantifying the phase change of the sample of polymeric recording medium “Difphen” during exposure of actinic radiation of 473nm.

It is shown that irreversible changes of the sample with the thickness of 2.7 mm under exposure of radiation of 473 nm with power (20÷36) mW at full transformation of PQ into PP is characterized by the negative phase difference of testing radiation of 532 nm with a value of (1,0±0,1)π radian. The value of reversible changes, which due to thermal effects, is characterized by the positive phase difference of testing radiation of 532 nm which is estimated be the value ≈ 3π radian.

Thus, at these experimental conditions reversible changes of optical characteristics of a polymeric sample, that accompany the process of exposure of actinic radiation, greatly exceed irreversible changes that provide recording holographic information.

Perhaps these facts explain the failure of some experiments carried out before, including the authors, on recording of highly selective reflective holograms on samples of polymeric medium with diffusional amplification.

To reduce distorting influence of thermal effects during holographic recording it is necessary to choose conditions of the experiment associated with the increase of influence of phototransformation of PQ (selection of optimal working wavelength) and for reduce the influence of thermal effects (wavelength and power of exposed radiation, duration of exposure and etc.)

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