

Surface relief grating recording in azobenzene epoxy films

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In this work the direct one step formation of surface relief gratings (SRG) in azo-epoxy polymer films during holographic recording was studied. In this material azo-compound is covalently attached to epoxy forming polymer. The main advantages of azo-epoxy polymers are simple and cheap synthesis, low polymerization degree, thus the photo-induced mass transport process has been facilitated. The dependence of SRG formation efficiency in AAB:BADGE films on sample preparation conditions, film content, recording parameters and possibility of reversible recording and SRG self-enhancement process was studied.

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1. Introduction

Azo-compounds have been under heavy investigation since 1995 when Rochon research group [1] announced surface relief grating (SRG) formation in azobenzene containing polymer films. Films possess good light induced anisotropy and can be successfully used in micro and nano patterning. There are two possible ways to prepare azo-dyed polymer film: azo-compounds can be mixed with polymer chain forming “guest-host” system and azo-dye can be covalently attached to the main polymeric chain. “Guest-host” system has very low efficiency, since azo-dye is not able to move a polymeric chain in the presence of electromagnetic field produced by laser illumination. Better results were obtained using films with covalently attached azo-dye but preparation of such films usually is difficult and expensive.

In this work we produced films with azo-dye covalently attached to the main polymeric chain, using amino-azo-dye and epoxy resin as a polymer. In epoxy resin and amino-azo-dye system under the thermal treatment the oxyrane ring opening reaction is induced and as a result azo-dye and the polymer chain can be covalently connected. The reaction proceeds with high efficiency [2,3]. We studied SRG formation dependence on thermal treatment and recording parameters in obtained films.

2. Experimental

2.1. Holographic set-up

We used classic holographic set-up where laser beam was split into two equal intensity beams by beam splitter [4]. We studied holographic recording in azo-epoxy films by +45/-45 linear polarization state of recording beams.

Using this polarization state holographic recording was the most efficient, we tested it and it was described by many researchers before [5-7]. Before beam splitter lens was placed in order to expand a laser beam for obtaining uniform illumination. Intensity of recording beams was varied from $I = 16 \text{ mW/cm}^2$ to 1200 mW/cm^2 . Diffraction efficiency was monitored by 1st order diffraction maximum of recording beam in reflection mode. In this case diffraction maximum gives information mainly of surface relief grating (SRG) formation and neglects photoinduced processes in the volume of the film.

2.2. Sample preparation

Usually synthesis of covalently attached azo-dye to the main polymeric chain is difficult, expensive and requires further purification. In this work we used simple oxyrane ring opening reaction to obtain material where azo-dye is covalently attached to the main polymer chain. This reaction takes place under thermal treatment of epoxy resin and azo-dye mixture and aminoazo-dye works as a hardener for epoxy resin.

We used classic epoxy resin Bisphenol A diglycidyl ether (BADGE) as received from Sigma-Aldrich and mixed it with 4-Aminoazobenzene (AAB) purchased at Sigma-Aldrich, in acetone or toluene. After applying on the glass substrate, samples were placed in oven for thermal treatment 20 - 72 h. Thermal treatment after film applying on the substrate made the film uneven with high difference of sample thickness. To avoid this, we heated the mixture of ABB and BADGE. Then we dissolved it again in 2,4 ml acetone and applied on the glass substrate. Film was uniform, optically homogenous, but process of surface relief formation was the same at both samples – heated after or before applying on the glass plate.

Rigidity of the film have proportional dependence on index of chain length but it strongly depends on molar

concentration of both components – azodye and epoxy resin. To investigate this dependence samples with molar concentration ratio $n_{\text{azo}}:n_{\text{epoxy}} = 5:2; 2:1; 3:2; 1:1; 1:2$ were prepared. When molar concentration n ratio is $n_{\text{azo}}:n_{\text{epoxy}} = 1:1$ AAB attaches to one of oxirane groups and open the second oxirane group allowing to form long-chain polymer with high efficiency [2]. When molar concentration ratio reaches $n_{\text{azo}}:n_{\text{epoxy}} = 2:1$ low- weight molecular glass can be formed when each oxirane group attaches one aminogroup [8]. With ratio $n_{\text{azo}}:n_{\text{epoxy}} = 5:2$ AAB molecules must be left in material in unattached form, and participate in photoinduced processes as “guest” molecules [9-10]. If ratio is under $n_{\text{azo}}:n_{\text{epoxy}} = 1:1$ there is not enough AAB molecules and some BADGE molecules must be unattached or without AAB in polymeric chain.

3. Results and discussion

By FTIR spectroscopy we investigated whether the polymerization reaction takes place in prepared samples. We measured FTIR spectra of BADGE solution in acetone, AAB solution in acetone and thermally treated AAB-BADGE film for 24h at 100° C sandwiched between two Si wafers. In the Fig. 1 we can observe two peaks in the range 3500 – 3250 cm^{-1} , characteristic for primary amines (AAB). After thermal treatment there is only one intensive peak, characteristic to secondary amines (AAB-BADGE) and it is strong conformation of reaction between AAB and BADGE [2-3]. As well in the Fig. 2 it can be seen epoxy ring peak at 911 cm^{-1} decrement after thermal treatment and bands characteristic for C-N and C-O-C bounds what forms after reaction between AAB and BADGE [2]. In addition no sensitizers are required for reaction between BADGE and AAB.

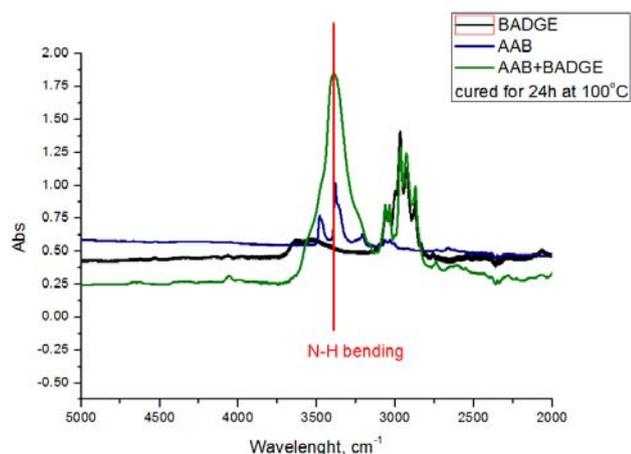


Fig. 1. FTIR spectrum of AAB-Badge film in the 5000-2000 cm^{-1} range

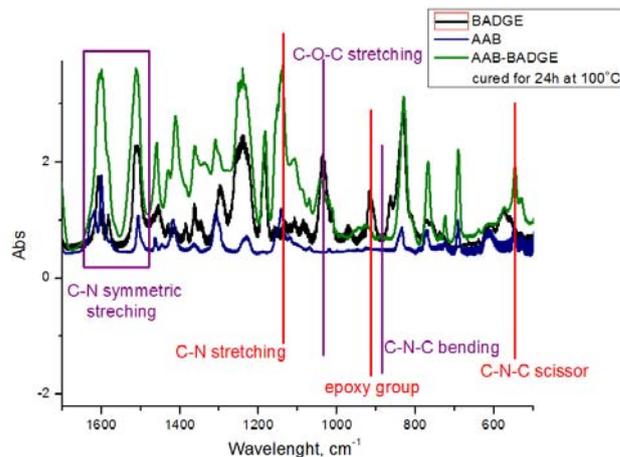


Fig. 2. FTIR spectrum of AAB-Badge film in the 1700-500 cm^{-1} range

We studied thermal treatment temperature influence on holographic recording in BADGE:AAB films (Fig. 3). We used sample with molar concentration ratio $n_{\text{azo}}:n_{\text{epoxy}} = 2:1$ and heated it in oven for 24h at different temperatures. If temperature was below $T = 90^\circ \text{C}$, film with good optical quality couldn't be obtained. Ring opening polymerization reaction didn't proceed completely what can be concluded by film rigidity; it remained sticky similar to pure BADGE and couldn't be used for recording. If samples were heated longer (up to 72 h) the samples of good optical quality were obtained even at 70° and 80° C but preparation time of such films are too long. The best results were obtained with the films heated at 90° – 100° C for 24 h. Further increment of temperature decreases SRG formation velocity. At higher temperatures rigidity of the film and free surface energy is too high. It can be explained by longer polymer chain formation. At these conditions more energy for mass transport is required, thus, surface relief formation is inhibited.

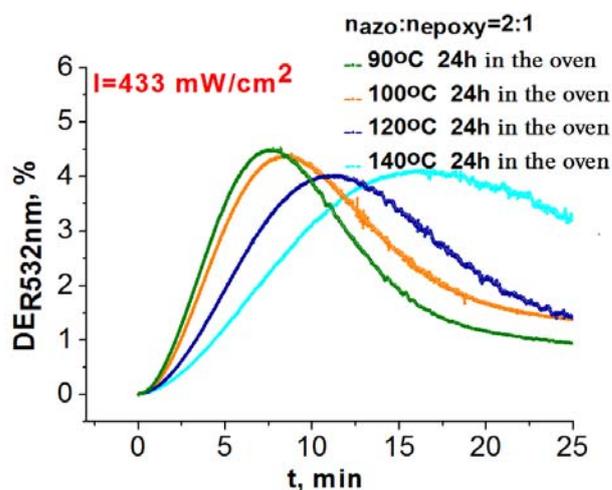


Fig. 3. Annealing temperature influence on holographic recording in BADGE:AAB films

For study on molar concentration ratio we used the samples with $n_{\text{azo}}:n_{\text{epoxy}} = 5:2; 2:1; 3:2; 1:1; 1:2$ and thermally treated them in the oven for 24h at 100° C and for 72h at 80° C. The obtained results were similar for both treatment conditions (Fig. 4). The highest SRG formation velocity – $\text{tg}\alpha$ [4] was obtained using $n_{\text{azo}}:n_{\text{epoxy}} = 2:1$. In this case polymeric chain is the shortest and mass transport is the most effective. At molar concentration ratio $n_{\text{azo}}:n_{\text{epoxy}} = 5:2$ mass transport could be slightly hindered by spare of AAB molecules. If number of AAB molecules per one epoxy molecule is below two, velocity of recording significantly decreases due to longer polymeric chain formation.

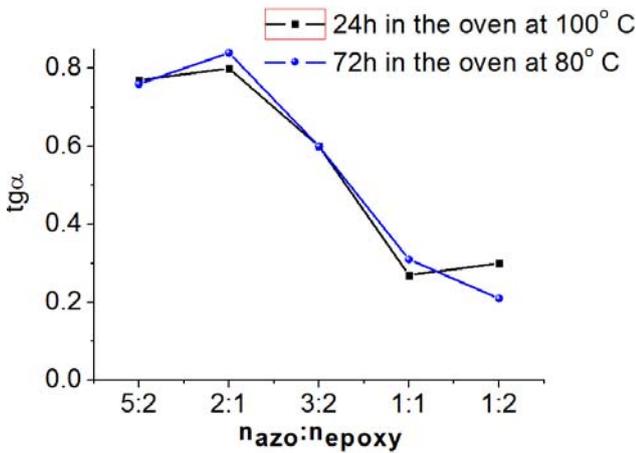


Fig. 4. SRG formation velocity dependence on molar concentration ratio

The studies of holographic recording dependence on intensity of recording beams (Fig. 5) showed that in the intensity range of both recording beams 15.8 mW/cm² – 1183 mW/cm² the recording efficiency depends only on exposure dose ($E= I t$). It is very convenient for practical application. It is easy to calculate exposure required to record relief grating with defined depth. AFM study allowed to estimate SRG formation velocity and required exposure. Value of SRG formation velocity is the highest in the beginning of recording, when DE value increases, after DE reaches maximal value, velocity slightly decreases, but SRG formation continues. It corresponds to well known formula [11] for phase holograms:

$$\eta = \sin^2(\pi \Delta n h / \lambda \cos \phi) \quad (1)$$

where η —diffraction efficiency, Δn — refractive index modulation, h — grating height, and ϕ — angle of incidence.

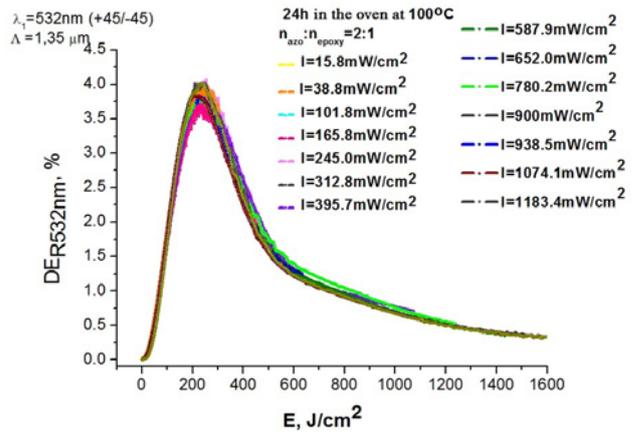


Fig. 5. Holographic recording dependence on intensity of recording beams

We measured the depth of SRG by AFM after some received exposure [13-14] (Fig. 6). SRG depth reaches its maximal value when DE curve saturates and there are no further changes in DE value or SRG depth. Obtained SRG is perfectly uniform, without any irregularity.

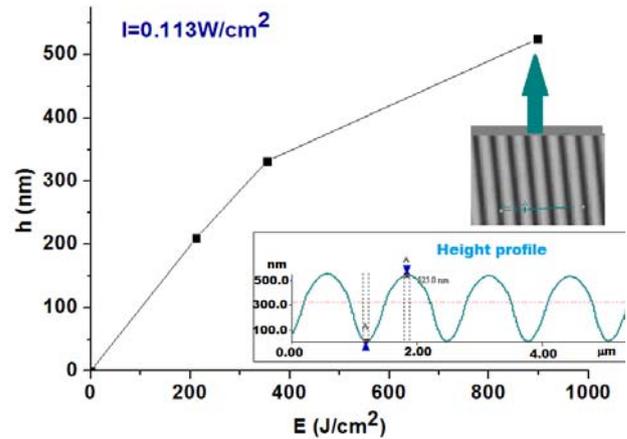


Fig. 6. The dependence of SRG depth on exposure dose and AFM picture of recorded grating

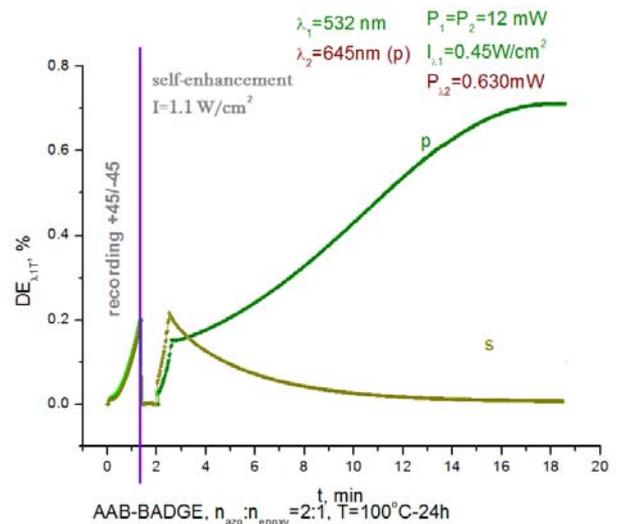


Fig. 7. Self-enhancement process in AAB:BADGE film with different polarization states of recording beam

We observed SRG self-enhancement process in AAB-BADGE film. After recording of SRG by +45/-45 linear polarization with DE of 0,2% in reflection mode state, we switched off one of recording beam, changed polarization state of another beam to “p” or “s” linear polarization. We increased intensity of the beam 5 times – from $I_{\text{beam}} = 0.22 \text{ W/cm}^2$ to $I_{\text{beam}} = 1.1 \text{ W/cm}^2$. Without intensity changes, self-enhancements process is much slower and less effective.

Self-enhancement process was observed using “p” polarized recording beam. Diffracted beam from initial grating interferences with recording beam and creates interference pattern which correspond to interference pattern produced by p-p polarization state in two-beam holographic recording, only contrast of the grating is much lower and it changes during the recording due to increment of intensity of diffracted beam. P polarized one recording beam produces SRG similarly to two p-p polarized beams. Initial diffraction efficiency increased 4 times, but the depth of the SRG according to AFM measurements increased 5.3 times – from $h = 32 \text{ nm}$ to $h = 170 \pm 10 \text{ nm}$.

If we use “s” polarized recording beam with increased intensity, no self-enhancement process can be observed, contrary, SRG erases. Since s-s two-polarized beam can't produce SRG on the surface of AAB:BADGE film, self-enhancement process can't be observed and SRG erases. At the same time, we can't obtain smooth surface instead of SRG, but structures as it seen on Fig. 8 forms on the surface. SRG erases because of material softening leading to SRG destruction. New SRG does not form due to lack of driving force necessary for SRG recording.

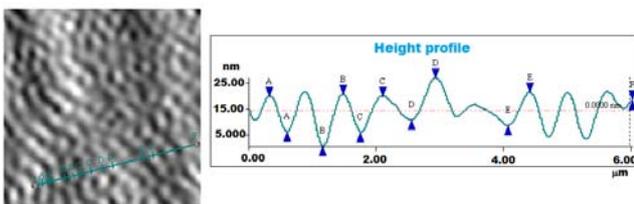


Fig. 8. Surface profile of grating after self-enhancement process by s polarized recording beam

Using such erase method it is possible to obtain reverse recording in AAB-BADGE (Fig. 9). We can repeatedly record SRG. Recording velocity $\text{tg}\alpha$ [15] decreases in every next recording from $\text{tg}\alpha = 0,267$ in the first recording to $\text{tg}\alpha = 0.008$ in fourth recording. Further recording become less effective because surface of the sample in the beginning of recording is not smooth and additional energy is necessary to erase previous structures.

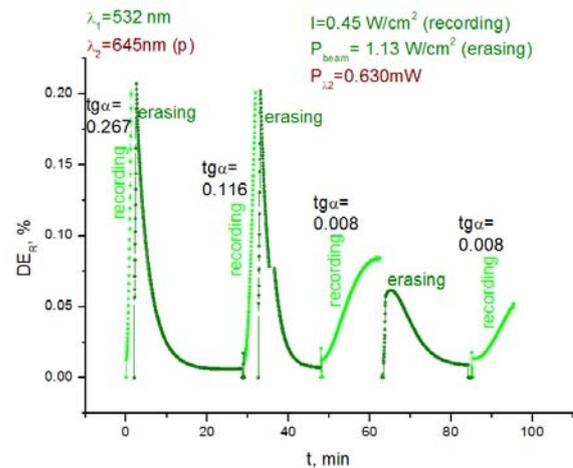


Fig. 9. Reversible recording in AAB:BADGE

4. Conclusion

AAB:BADGE films is promising material for micro and nano patterning due to its low costs and easy synthesis. In ABB:BADGE films it is possible to record good quality surface relief grating, but the efficiency of recording strongly depend on film preparation conditions. Optimal heating parameters are 100°C for 24h. During this time BADGE and AAB form good optical quality film suitable for surface relief patterning. Intensity of record beam in the range from $I = 16 \text{ mW/cm}^2$ to 1200 mW/cm^2 does not influence DE of grating, and DE_{max} is reached after exposure by a dose of $E = 200 \text{ J/cm}^2$. It is easy to calculate exposure for required DE value, since there is no dependence on intensity of recording beams.

Self-enhancement of SRG was observed in AAB:BADGE films. An increase of SRG depth 5.3 times after holographic recording was obtained by one p-polarized beam illumination.

It is possible to record grating repeatedly in AAB:BADGE film. Grating can be erased by s-polarized one recording beam. We can obtain the same high of SRG, but each time exposure for SRG formation has to be grater.

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