Holographic property of photopolymers with different amine photoinitiators*

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Holographic parameters and photobleaching kinetics of the photopolymers with five different amine photoinitiators are studied. The maximum values of diffraction efficiency, photobleaching coefficient and quantum yield follow the sequence: Triethanolamine (TEA)> Diethanolamine (DEA)> Ethanolamine (EA)> Triethylamine (TETN)> Diethylamine (DETN). The holographic capabilities of photopolymer performances are determined by the number of functional groups in the amine molecular structure. There is an optimum proportion of the photoinitiator, the photosensitizer and the monomer in the test of holographic parameters with different amine concentrations. The maximum diffraction efficiency is 59.26%, sensitivity is 1.72×10^{-3} cm^2/mJ, and the maximum refractive modulation index is 4.64×10^{-4}.

Keywords: photopolymer, amine, holographic recording, photoinitiator

PACC: 4270J, 4280T, 4240K

1. Introduction

With the rapid development of information technology, the current storage methods cannot satisfy one's demands for huge capacity and high speed storage facilities, so the digital holographic storage with high signal-to-noise ratio, high storage capacity, and parallel processing characteristics has become the major technique being developed nowadays. In recent years the interests in photopolymers as holographic recording materials have increased dramatically. The main reason is that these materials have many advantages such as high diffraction efficiency, easy preparation, low noise, real-time processing and low cost.[1,2]

A classic holographic photopolymer usually consists of one monomer or a mixture of monomers, a photosensitizer, a photoinitiator, and a polymeric film-forming binder. In this procedure of photopolymerization, one of the major difficulties is to design a high-efficiency initiation system to improve the holographic properties of the material in order that it could be applied to the digital holographic storage.[3,4]

Amidocyanogen group in photoinitiators neither absorbs the radiation energy, nor causes polymerization. However, they can lift the efficiency of the photoinitiator to increase the speed of solidification to a large extent.[5] In the present article we study the effect of different photoinitiators containing amidocyanogen and the photobleaching mechanism by measuring the dynamic trace of diffraction efficiency and the transmission of the photopolymers including different photoinitiators.

2. Experimentation

2.1. Sample preparation

Our system is composed of binder polyvinyl alcohol (PVA), monomer N, N'-methylenebisacrylamide (BAA) and acrylamide (AA), sensitizer methylene-blue (MB). The amine such as TEA, DEA, EA, TETN, DETN was used as the photoinitiators in our experiment.

All the materials were of the best available grade and were directly used without further purification. All the samples were prepared under normal laboratory conditions [20 °C–25 °C; relative humidity (RH) 40%–60%] as follows:

(i) The 2-g basic polyvinyl alcohol (PVA) material was dissolved in distilled water heated to 80 °C to

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yield a PVA aqueous solution with 10 wt% of PVA.

(ii) A monomeric solution was prepared by dissolution of 0.6-g acrylamide (AA) and 0.2-g N, N'-methylenebisacrylamide (BAA) into appropriate distilled water and heat to 30 °C with the addition of the corresponding volume of amine photoinitiators and the necessary amount of water to yield a homogeneous solution.

(iii) Crystals of methylene blue were dissolved in water to obtain the desired dye concentration.

(iv) Put all the monomer solution and 1-ml final dye solution into the PVA solution to obtain the photopolymeric solution. All operations were carried out in a darkroom, and solutions were prepared by adding components to the coating solvent and mixing with a mechanical stirrer until they dissolved completely.

We prepared a thick layer by pouring the photopolymeric solution over a 6 cm×6 cm×1 mm glass plate and adjusting the layer thickness. The layer was placed in dark room under normal laboratory conditions for 24–48 h (drying period) and the thicknesses of the photopolymeric films obtained were measured to be approximately 270–300 μm by using a micrometer caliper.

2.2. Experimental apparatus

The basic setups used in our experiment are shown in Figs. 1 and 2. In the figures, H denotes holographic plate; BS stands for beam splitting and M_i ($i = 1, 2, 3$) refers to mirror, two vertical plane polarized light beams with equal identities are obtained by adjusting the mirror appropriately; SF stands for spatial filter; L_1 and L_2 represent Fourier lenses each with the focus length f; SH denotes shutter; PM stands for power meter. In our experiments, an He–Ne laser with a wavelength of 632.8 nm was used as a light source, because there is a strong absorption in the red light area in the absorption spectrum of the aqueous solutions of MB.

When investigating the optical transmission properties of the photopolymer film (shown in Fig. 1), we split the light source into two beams with an intensity ratio of 1:1 by BS, i.e. the intensity of each beam is 32 mW/cm^2. Firstly, we shut off SH_2 and let only one beam pass through the sample. Thus all the transmitted light is recorded by the PM. And then, we shut off SH_1 to record the intensity of the incident light. The laser beam was focused on the sample with a 120-mm focal length. Accurate control of exposure is usually achieved by a 4f system which is used to insure that the place where the laser beam irradiates the photopolymer film does not change with the angle of the reading beam.

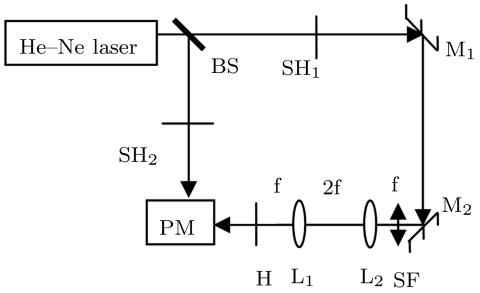


Fig. 1. Schematic setup for the testing of transmission.

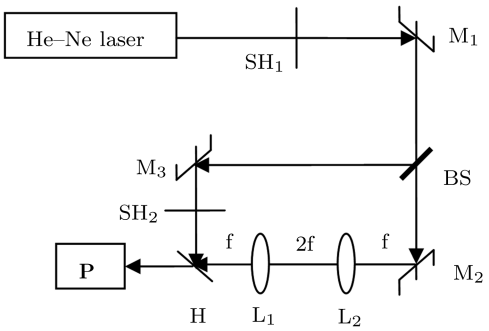


Fig. 2. Schematic setup for the testing of diffraction efficiency.

Similarly, when measuring the optical diffraction properties of the photopolymer film (shown in Fig. 2), we let the beam from M_2 act as the object beam, and from M_3 serve as the reference beam. After adjusting two beams to overlapping on the sample plate, we shut off SH_1 and SH_2 to record the incident light power and the first level diffraction power by PM, respectively.

3. Results and discussion

3.1. Theoretical model

Because amine is commonly used as a hydrogen (H) provider, we use the following theoretical model to analyse the contribution of the amine photoinitiators to the holographic recording efficiency of the photopolymer:

$$\mathrm{DYE} \xrightarrow{h\nu} {}^1\mathrm{DYE}^* \rightarrow {}^3\mathrm{DYE}^*,$$

$$^3\mathrm{DYE}^* + \mathrm{ED} \rightarrow \mathrm{LDYE} + \mathrm{Am},$$
$$^3\mathrm{DYE}^* + \mathrm{Am} \xrightarrow{k} \mathrm{DYE}^{\bullet} + \mathrm{Am}^{+\bullet},$$
$$^3\mathrm{DYE}^{\bullet} + \mathrm{Am} \xrightarrow{k} \mathrm{DYE}^{-} + \mathrm{Am}^{+\bullet},$$
$$\mathrm{Am}^{+\bullet} \xrightarrow{-H^{\oplus}} \mathrm{Am}^{\bullet},$$
$$\mathrm{DYE}^{-} \xrightarrow{+H^{\oplus}} \mathrm{LDYE}.$$

Fig. 3. Scheme of the proposed reaction mechanism for the studied photopolymerization. DYE: photosensitizer; ^{1}DYE*: excited photosensitizer; ^{3}DYE*: triple state excited photosensitizer; DYE$^{\bullet}$: photosensitizer derivative radical; DYE$^-$: photosensitizer anionic derivatives; LDYE: leuco-dye; Am: amine; Am$^{+\bullet}$: amine cationic radical; Am$^{\bullet}$: amine radical derivatives; $h\nu$: the energy of an incident photon; k: reaction constant.[6]

When the photosensitizer was exposed to the light, the molecules of the photosensitizer were excited: electronics in low-energy orbit might absorb a photon to jump into an unoccupied high-energy orbit, that is, n–π^* jump. However, in this process the self-spin state of electronics did not change, and the molecule was in the single excitation state (the mechanism of the reaction is described in Fig. 3). The lone pair electrons transferred from the single excitation state to the triple excitation state which is more stable and lasts longer, via in-state jump. After the dye molecules absorbed energy and jumped to the excitation state, photoinitiator absorbed the energy from the molecule in the triple excitation state and became amino radicals which initiated the formation of polymerization.[7,8]

3.2. Effect of different amine-photoinitiator

Photoinitiator is one of the most important components of photopolymer. It has a direct influence on the optical record capability of the last hologram. In order to make the photopolymer film have the excellent holographic characteristic, it should satisfy the following two conditions: one is the polymeric capability of the photopolymer. Polymerization can take place quickly while photoinitiators cause free radicals to be created for the purpose of quickening transfer speed; the other is the higher refractive index modulation, in order to increase the diffraction efficiency of photopolymer.

A comparison among curves of transmission versus exposure time for five amine photoinitiators (shown in Fig. 4). In this figure we can see that the transmissions of photopolymer based on different amine photoinitiators, under 633 nm, increase gradually as time goes on, and the transmissions each arrive at a saturation value finally after reaching a maximum of transmittance. From theoretical model we can conclude that in the beginning, polymerization reaction arises by the ground state free radicals because of the energy transferring between the donor molecule (the photosensitizer) and the acceptor (the photoinitiator). Along with the photochemical reaction unceasingly taking place between the dye and the initiator, the concentration gradually reduces and the monomers are polymerized continuously. Finally, polymeric film is solidified, and then the process of electron migration between the dye and the amines becomes more difficult. Photosensitizers are bleached completely finally. The transmission reaches the maximum, and arrives at a stable saturation value.

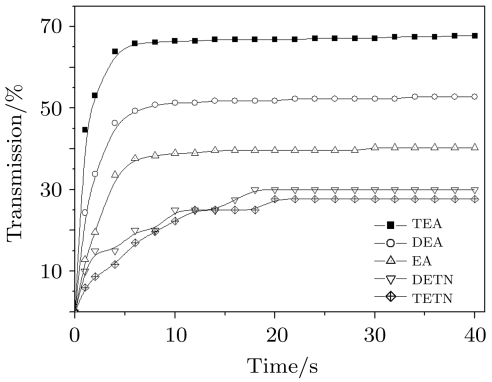


Fig. 4. Transmissions versus exposure time for different photoinitiators.

The sequence of magnitude for final transmission, quantum yield, and photobleaching coefficient of photopolymer is TEA>DEA>EA>TETN>DETN (shown in Figs. 4 and 5). We obtained the above parameters numerically by using the fitting procedure described in Ref. [9]. The differences in photobleaching coefficient among these photopolymers are not distinct, but the difference in quantum yield between TETN and DETN is prominent. The quantum yields of TETN and DETN are 9.456×10^{-5} mol·Eeinstein^{-1} and 5.738×10^{-5} mol·Eeinstein^{-1} respectively. It shows that a variety of the amine molecule structures have great effects on quantum yield and photobleaching coefficient of photopolymers based on dif-

ferent amine photoinitiators, and for TEA, there exist three hydroxyl groups in the structure, in which the efficiency of radical polymerization can increase to a large extent. And the amine molecule structure also affects the velocity of the photopolymerization of alkene monomer. The efficiency of radical polymerization is mainly determined by the lively level of the hydrogen on the nitrogen atom close together with carbon atom. Because the hydrogen atom activity will affect the velocity of the proton shift, and it also determines the level of difficulty in producing the high active amine free radical.

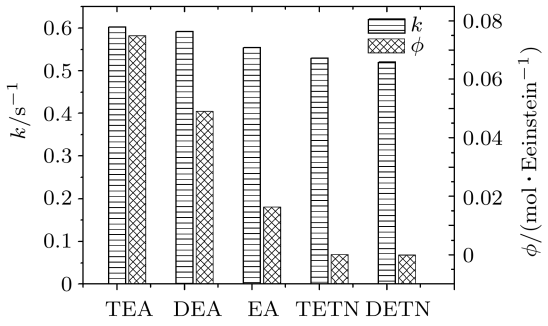


Fig. 5. The values of quantum yield ϕ and photobleaching coefficient k for different photoinitiators.

For the remainder of this paper, we determine the diffraction efficiency η, the exposure sensitivity S and the refractive index modulation Δn as follows:

$$\eta = I_d/(I_i - I_r), \tag{1}$$

$$S = \sqrt{\eta_{\max}}/E, \tag{2}$$

$$\Delta n = \sin^{-1}(\eta_{\max})^{1/2}\lambda\cos\vartheta/\pi d,^{[10]} \tag{3}$$

where I_j ($j = d$, i and r refer to the diffractive, the incident and the reflective beams respectively) is the intensity of the beam, $\eta_{\max}$ is the maximum value of the diffractive efficiency, E is the average exposure energy, λ is the wavelength of the incident beam, ϑ is the incident angle, and d is the thickness of the sample.

We can see from Fig. 6 and Table 1 that when the photopolymer is initiated by the TEA, the diffraction efficiencies are maximal for all these photopolymers based on different amine photoinitiators, and the maximum diffraction efficiency is 51.4%. But the maximum diffraction efficiencies of DEA and EA are 43.27% and 43.8% respectively, and they are both lower than that of TEA. The maximum diffraction efficiencies of other two kinds of amine photoinitiator are much lower, although dye molecules can be bleached in recording process also. This is because the phenomena appear in TETN and DETN where water is absorbed on the sample surface seriously compared with other three kinds of amines. The hydrophilicity of the material is very strong, but compatibility with environment is too bad. The high humidity of environment makes it more difficult that the photopolymer film comes into being. The diffraction efficiency decreases significantly, this is because there is the scattering during the exposure due to the water on the sample surface.

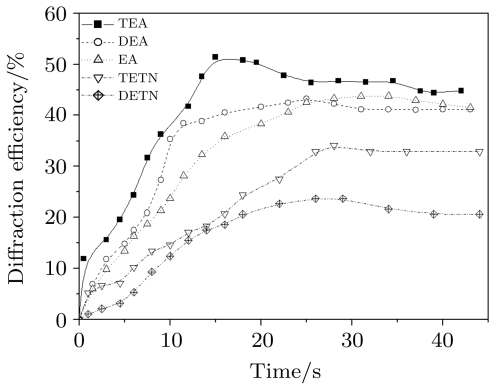


Fig. 6. Diffraction efficiencies versus exposure time for different photoinitiators.

Table 1. Holographic parameters of photopolymer for different photoinitiators.

Photoinitiator	$\eta_{\max}$/%	S/(cm^2/mJ)	Δn
TEA	51.4	1.494×10^{-3}	0.422×10^{-3}
DEA	43.27	0.822×10^{-3}	0.379×10^{-3}
EA	43.8	0.608×10^{-3}	0.382×10^{-3}
TETN	34.1	0.652×10^{-3}	0.329×10^{-3}
DETN	23.7	0.585×10^{-3}	0.268×10^{-3}

There are hydroxyl groups and amine groups in the structures of TEA, DEA and EA, but there exists only one kind of amine group in the structures of TETN and DETN separately. From Table 1 we can see that in the test of holographic parameters of photopolymers sensitized by MB based on different amine photoinitiators, the photopolymer initiated by TEA with three hydroxyl groups and a tertiary amine group in the structure shows a better performance on exposure sensitivity and refractive index modulation than those of another samples.

This is because the hydrogen of hydroxyl of TEA is the most lively and it is extremely easy to be lost.

The triply excited photosensitizer can rapidly produce the exciplex with the TEA, and the production: α-amine free radicals are able to initiate the amide monomer polymerization effectively. Therefore the photosensitive system with TEA is the extremely effective one with respect to the amide monomer polymerization in air. Because of the dissimilarity of the molecular structures and the number of hydroxyl group in the molecular structure, the abilities for different molecules to provide the free radicals of the initiator are different, thereby causing the difference in holographic parameter.

We can draw a conclusion that why this kind of photosensitive system can initiate photopolymerization in the air is because of the high activity between the excited photosensitizer and the hydrogen donor and the lively free radicals produced by the hydrogen donor. The α-hydrogen of amine is more lively and the free radicals of amine are easier to form, so the effect of initiator is better. Certainly, when we choose amines as initiator, we also must consider the stability and solubility and so on.

3.3. Effect of different TEA concentrations

It is shown in Fig. 7 a comparison among the transmissions versus exposure time for different concentrations of TEA. In the case where the concentration is 0.38 M, the transmission becomes maximal finally. When the concentration is larger or smaller, all the transmissions reduce more or less, and the times to reach their saturation values are also different.

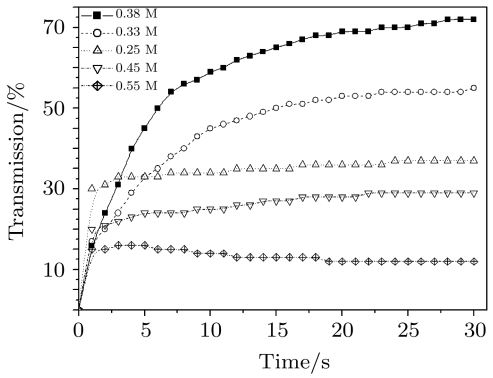


Fig. 7. Transmissions versus exposure time for different TEA concentrations.

Along with the increase of the concentration of TEA, the quantum yield descends, after achieving the minimum, the velocity of the polymerization increases on the contrary (shown in Fig. 8). The redox reaction of this photosensitive system is initiated at a very low quantum yield. However, the amines actually can cause the initiator to display the extremely high polymerization efficiency.[11] After achieving a certain concentration, when the concentration of TEA still increases, the primary free radicals increase per unit time, and the polymerization will be speeded up also. But the excess partial concentration of resultant of reaction will lead to the "cage effect", making the combination of free radicals terminated easily thus causing the quantum yield to descend.

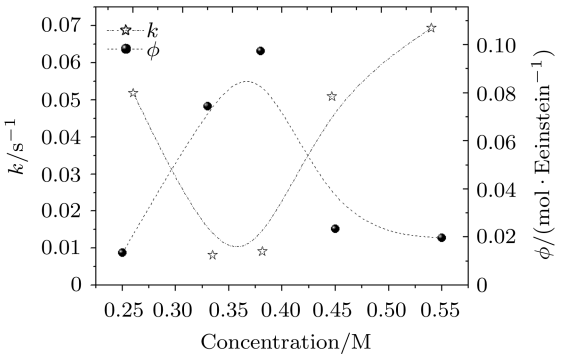


Fig. 8. The values of quantum yield ϕ and photobleaching coefficient k for different TEA concentrations.

In our experiment, the explanation for the decrease in transmittance of the material (shown in Figs. 4 and 7) is the occurring of the noise gratings caused by scattering centres in the sample. The formation of these centres is due to the precipitation of monomers on the surface of the film. This phenomenon is attributed to the formation of randomly distributing solid microparticles of BAA, which is the less soluble monomer, favoured by temporal evaporation of the water resident in the film. It has been observed that the precipitation of monomers is favoured when the concentration of monomers, specially BAA, is high and the ratio of PVA to monomers is low. When the age is increased, there is less water in the film and these particles are larger. At the same time, if the concentration of the amine is too much high, the amine possibly infiltrates from the interior of the thick film to the surface.[12] Thus we must pay attention to the balance of the ratio of the photoinitiator to the photosensitizer and the monomer in the formula, and use an appropriate concentration of amine

so as to avoid this phenomenon to an extent as great as possible.

When the TEA concentration is kept at 0.38 M in the system (shown in Figs. 9 and 10), the maximum diffraction efficiency is 59.26%, exposure sensitivity is 0.00172 cm^2/mJ and the refractive index modulation is 4.64×10^{-4}. When the concentration increases or diminishes, a variety of the final diffraction efficiencies appearing show a similar trend to that of the transmission (shown in Fig. 9). The ability of electron shift is determined by the interaction between amine photoinitiators and triple state excited photosensitizer, the structure of the amine, the ratio of the concentration between photoinitiator and photosensitizer, and so on. The weaker the ionization potential of amine is, the stronger the ability of electronic shift will be. It is shown that in the entire recording process there is an optimum proportion among the photoinitiator, photosensitizer and the monomer.[13,14]

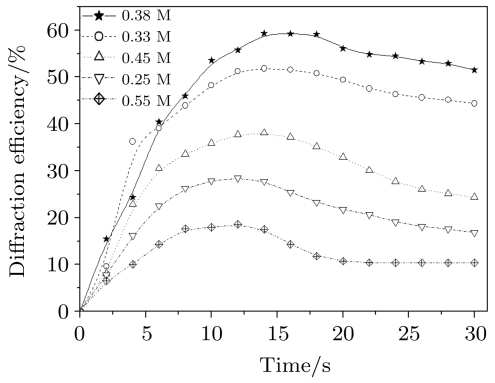


Fig. 9. Diffraction efficiencies versus exposure time for different TEA concentrations.

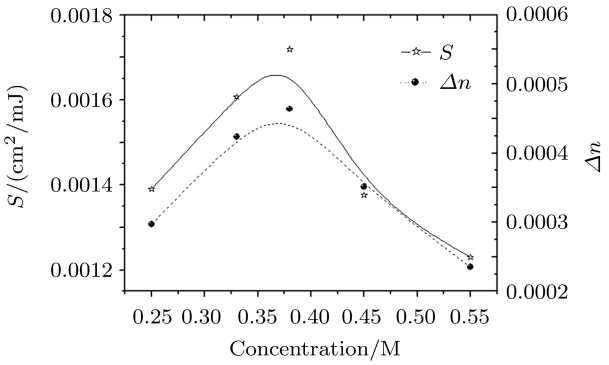


Fig. 10. Curves for exposure sensitivity and refractive index modulation for different TEA concentrations.

The function of amine in the mechanism of the photosensitive system mainly depends on that of the lively α–H in the amine molecule. And the quality of initiation effect is determined by the ability to provide the amidogen free radical of the amines in the holographic photopolymerization system to an extent as great as possible. The concentration of photoinitiator is very low in the system, and the photoinitiator molecules are surrounded by the "cage" of monomer and solvent. The primary free radicals produced by the photoinitiator inside the "cage" initiate the polymerization, only after their diffusing out of the "cage".[15] If they diffuse out too late, other reactions would take place possibly. The primary free radicals are combined again in the unit time because of the "solvent cage". This phenomenon is related to the structure of the photosensitizer. When the distance between the primary free radicals is shorter, the probability that free radicals are combined again is higher, and the quantum yield of photoinitiator is lower. The monomers in the dark area cannot diffuse into the bright area quickly in the sample, because the viscosity of the PVA is higher and the diffusion coefficient is lower, so that most of the excited photosensitizers return to the ground state or are combined with each other. The decrease of the photosensitizers makes the monomer polymerization insufficient, the diffraction efficiency drop off, and the capability of the material reduce.

4. Conclusions

Holographic parameters and photobleaching kinetics of the photopolymers with five different amine photoinitiators are studied by means of fitting the experimental data of transmittance to a function of time. Under the same condition of the other components, the sequence of maximum values of diffraction efficiency, quantum yield, and photobleaching coefficient of photopolymer is TEA>DEA>EA>TETN>DETN. In the comparison of holographic parameters, TEA is the best among these photopolymers initiated by different amine-photosencitizers. There is an optimum proportion under the same components in the photopolymerization. We can see from the abovementioned result, not all amine-photoinitiators have the good initiation effectiveness. Only when there are more functional groups in the amines structure, as well

as more lively α–H, can the amine-photosencitizer possibly play a better role in the photopolymerization.

All these parameters are advantages to analysing the photochemistry dynamic process of this kind of holographic material, and important for optimizing the holographic photopolymer as a reference.

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