Temperature effect in PQ:PMMA photopolymer

Shiuan-Huei Lin and Ken Y. Hsu[a]
Department of Electrophysics
[a]Institute of Electro-Optical Engineering
National Chiao Tung University
Hsin-Chu, Taiwan, R.O.C.

ABSTRACT

We present our studies on the temperature effect of the grating recorded in a phenathrenequinone (PQ) doped poly(methyl methacrylate) (PMMA) photopolymer. The characteristics for recording a strong single grating have been studied. We find that the main limitation of full utilization of the refractive index modulation of the hologram is caused by the scattering effect. Experimental demonstration of using dark enhancement to enhance diffraction efficiency of a grating is presented.

Keywords: Photopolymer material, PQ:PMMA, Holographic data storage, Dark enhancement, Temperature effect.

1. INTRODUCTION

Recently, many experimental works of holographic data storage involving polymer-based recording materials have been performed [1-5]. In developing such recording materials, many aspects must be considered: high sensitivity, simple chemical development, good spatial frequency response, high diffraction efficiency, high optical quality and long stability of the material. Among them, high diffraction efficiency and low scattering noise are the most desired material properties that could enable the holographic data storage achieve high storage density, high image quality, and low bit error rate. To achieve these requirements, some special design and treatments for fabricating the polymer materials have been proposed and demonstrated [6-8]. Among these recording materials, dye doped poly (methyl methacrylate) (PMMA) is one of attractive candidates due to its high thermo-stability and high optical quality. Moreover, some recent researches have proven phenanthrenequinone (PQ) doped PMMA polymer to be very useful materials due to their excellent properties: to be easy to form a bulk with high optical quality and negligible photo-chemical shrinkage [9-10]. In this paper, we present our investigations on the temperature effect of the grating recorded in bulk blocks of PQ-doped PMMA. The blocks consist of PMMA, the host matrix doped with PQ molecules as the photosensitive element. We will first describe the material design strategy and the preparation for making the thick polymer samples with negligible shrinkage. Then, we will concentrate on discussing material scattering noise characteristics for holographic data storage. Finally, we will propose a method to avoid the scattering noise and enhance diffraction efficiency of a grating in PQ:PMMA polymer. will be experimentally studied and discussed.

2. DESIGNING STRATEGY AND MATERIAL PREPARATION

We first briefly describe our designing strategy for making bulk PQ:PMMA samples with minimal dimensional shrinkage. Most photo-polymer materials consist of a photo-polymerizable monomer, a photo-initiator, and a sensitizer in a polymer binder. During optical exposure, a few photons can initiate a chain reaction of photo-polymerizable monomer molecules, which causes a strong change of the refractive index to form a strong index hologram. Because a large number of monomer molecules are involved in the formation of the hologram, the material exhibits significant dimensional shrinkage. One possible way to alleviate this problem is to separate the photo-chemical reaction from the polymerization of the host monomer molecules. The host polymer matrix is used to support the polymer matrix; and the doped molecules are the photosensitive elements to form the refractive index holograms. The host polymer matrix in our sample is PMMA which is made from the thermal chain reaction of polymerization of MMA monomers by using thermal initiator azobisisobutyronitrile (AIBN). At the same time, the photosensitive elements, PQ molecules are doped uniformly in this polymer host matrix. During the material preparation (named as pre-polymerization), most of the monomer molecules have

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been polymerized to form the host polymer matrix. Only a few percentage of un-reacted monomer molecules are left and these molecules together with photo-sensitizers have been uniformly distributed in the host polymer matrix. The ratio of the residual MMA molecules in our PQ:PMMA polymers, as observed from thermal gravimetric analysis, was about 10%. The analysis result is shown in Figure 1. It can be seen that the thermally induced weight decreases in our sample show two trends as the temperature raises. Since the MMA molecules are much smaller than PMMA polymer, the de-composition temperature of the MMA is lower than that of the PMMA. Therefore, ~10% of the weight loss of the sample at below 304°C, as illustrated in Figure 1, is considered as the residual MMA molecules after the pre-polymerization. The rest part of the sample is PMMA polymer. Therefore, the recording mechanism of the holographic grating in our sample can be understood as the following. During the optical exposure, under light illumination the photo-sensitize molecules PQ absorb photons and become radicals such that they bond with those ~10% residual monomer molecules on a one PQ to one MMA molecule basis. This chemical reaction occurs primarily in the bright region. Free PQ and MMA molecules diffuse from the dark into the bright regions. Consequently, a difference between the refractive index in the dark region and that in the bright region is created, i.e. a phase grating is formed. Since a large refractive index change can be induced by this process and thus a strong phase hologram can be obtained. However, because the residual monomers and photo-sensitizers involved in the formation of the hologram are only a small fraction of the compositions, the host polymer matrix structure can be maintained during the optical recording. As a result, the dimensional shrinkage and the bulk refractive index change induced by the recording process are minimized.

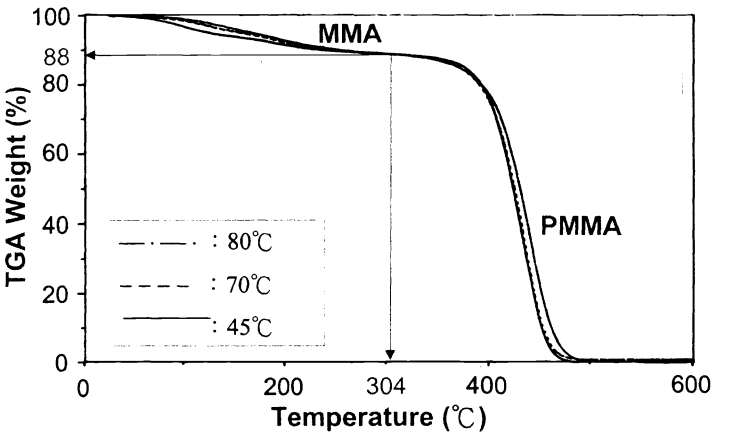

Figure 1 The results of thermal gravimetric analysis for different pre-polymerization temperature 80°C, 70°C and 40°C.

Next, we describe how to make the polymer sample with high optical quality. To obtain the high optical quality, some treatments to avoid the scattering particles and to reduce non-uniformities of the bulk refractive index are required. In the material preparation, the polymer blocks were made by two stages at different temperatures. Samples were prepared by dissolving the initiator, AIBN (~0.5%) and PQ molecules (up to 0.7%) in a solvent MMA and then was poured into a square glass tube. In the first stage, the samples were put in a pressure chamber at room temperature for about 120 hours until the solution turned into homogeneously viscid. During this stage, because of the slow polymerization rate at low temperature, nitrogen molecules released from the thermo-decomposition of AIBN and the heat produced from the chain propagation of the MMA monomers could leave the glass tube completely. Therefore, there were no residual air bubbles left in the sample. In the second stage, the temperature of the chamber was elevated to 45 °C for 24 hours to accelerate the thermo-decomposition rate of AIBN. Chain reaction was accelerated and the polymerization was completed. The sample then became a solid block with high-optical-quality.

3. OPTICAL CHARACTERISTICS OF THE SAMPLES

3.1. The optical quality of the sample

Our PQ:PMMA samples appear to be clear yellow color, with good optical quality and uniform transmission. We have measured the optical transmission of the different thick samples in the visible range. The samples possess strong absorption

below blue wavelength (<450 nm). They are totally transparent as the wavelength is larger than 540 nm. In the following experiments we used an agron laser with the wavelength 514.5 nm. At this wavelength, the absorption of 1.2-mm-thick sample is ~30.2% and that for the 2.4-mm-thick sample is ~44%.

To study the optical quality of our sample, we illuminate 4.8-mm-thick sample using a USAF resolution test chart image. Figure 2 shows the photograph of a directly transmitted image, in which the sample is placed near Fourier plane of imaging lens. It can be seen that the image retains clear fidelity, which is down to the number 6 of the group 5. The distortion of the image and scattering background noise are not obvious. In our system, this resolution seems to be around 95 lps/mm, which is close to the limitation of our CCD. For the application of volume holographic storage, thousands of pages are superimposed on a single location of a thick recording material. As the number of recording pages becomes large, the diffraction efficiency of each hologram is very weak (typically less than 10^{-6}) and particular attentions must be taken to keep material scattering noise to be minimum. Thus it is very important to grow a material with high homogeneity in the refractive index. In this aspect, our technique of pre-polymerization before the photochemical reaction seems to produce satisfactory index uniformity inside the sample to perform high density holographic storage.

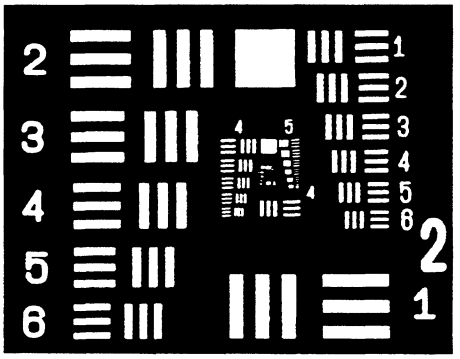

Figure 2. Photograph of a directly transmitted image through a 4.8-mm thick block

3.2. The dynamics of recording a holographic hologram in the sample

In order to explore the capability of our PQ:PMMA samples for holographic memory, we have measured the dynamic range of the refractive index of a 4.8-mm thick sample. Two beams of collimated light derived from an argon laser were symmetrically incident into the sample with an intersection angle of 32 degrees outside the sample. The grating diffraction efficiency is measured in real-time by use of a weak 632.8-nm He-Ne-laser beam at Bragg-matched angle. The resulting curve is shown in figure 3. It is seen that the diffraction efficiency reaches the maximum of 60% for the exposure energy of 0.3 J/cm^2 and then it begins to drop for further exposure. At this moment, we also saw a distorted pattern of the transmitted beams. We believe that this drop effect of the diffraction efficiency is caused by the fanning gratings, that are induced during the recording procedure. In the thick samples, the scattering beams induced by the scattering centers or the non-uniform refractive index have long interaction length. As a result, the local index change due to noise gratings are accumulated and become strong. Thus, most energy of the incident light is scattered into scattering beams and the directly transmitted beams are distorted very seriously. Comparing the picture in Figure 2 with that after 100-seconds illumination, it can be found that scattering effect causes a serious distortion to the transmitted image after long exposure. The implication of the scattering effect on holographic data storage is that the exposure time for each recording cannot be too long, otherwise image distortion occurs. Therefore, we have proposed an exposure schedule to avoid the long term exposure at a single location of the photopolymer for achieving multiple holograms storage in our sample.

Tin order to be able to calculate the upper limit of each exposure time, we have performed an experiment to investigate the scattering effect quantitatively. A collimated laser beam with 4 mW/cm^2 and 6-mm diameter was incident on the PQ:PMMA block. We measured the transmitted power inside the incident beam geometry as a function of time. As more exposure continued the directly transmitted power became less and less. If we defined the scattering ratio as the total power scattered outside the beam geometry divided by the initially transmitted beam power, then the dynamics of the fanning is shown in Figure 4. It can be seen that the scattering ratio is almost close to 70% after the exposure energy of 2.08 J/cm^2. This implies

that, in order to avoid the buildup of the fanning beam, the total exposure of a single recording should not be greater than 2.08 J/cm^2. This sets up an upper limit for the single exposure time.

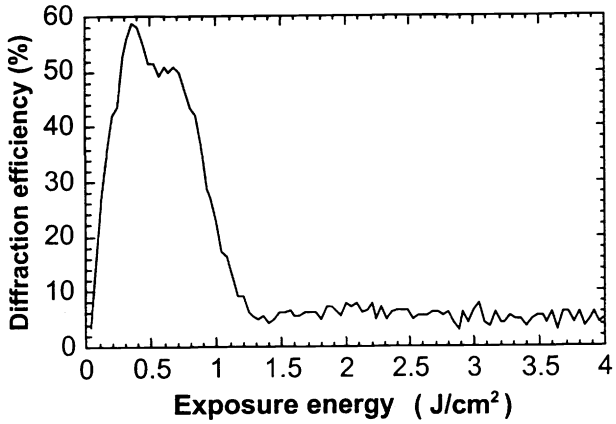

Figure 3. Recording dynamics of a single grating in 4.8-mm-thick polymer sample.

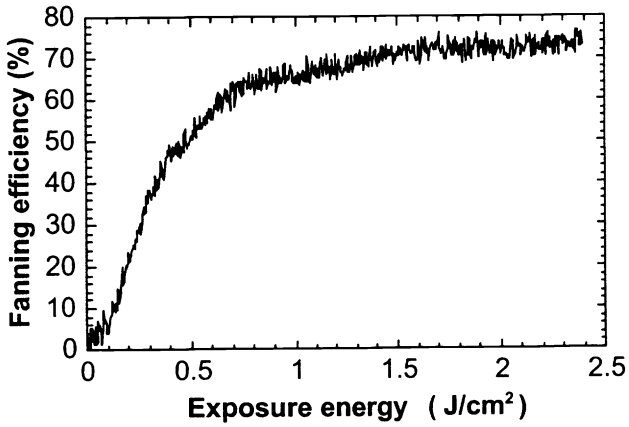

Figure 4. Dynamics of the fanning grating formation for 4.8-mm thick sample.

4. THE ENHANCEMENT OF HOLOGRAPHIC GRATING

4.1. The dark enhancement of grating

In order to avoid decrease of the diffraction efficiency which is induced by scattering, one should try to avoid the formation and cumulating of the scattering noise gratings. One possible way is to enhance the refractive index modulation by using the post diffusion of the MMA molecules following the photo-chemical reaction of optical exposure. The ides behind this is that the refractive index modulation of our photopolymer hologram can be greatly enhanced by a dark follow-up procedure. The method to achieve this is that after recording exposure, both writing beams were blocked and the hologram was kept in the dark for few hours to wait the un-reacted free PQ and MMA molecules to diffuse from the dark into the bright regions. Consequently, more difference between the refractive index in the dark region and that in the bright region can be created. Because the noise gratings formed during optical exposure is such weak that the diffusion of the residual MMA and PQ involved in this post formation of the hologram is negligible. As a result, the refractive index change of the noise grating induced by the recording light are minimized and the diffraction efficiency of the signal grating can be greatly enhanced.

Figure 5 shows the schematic diagram of the experiment setup for studying the dark enhancement of our photopolymer hologram. Two collimated 514-nm laser beams from an argon laser were used for writing a hologram in our PQ:PMMA photopolymer with the thickness of 1.2 mm. The intensities of those two beams were 1.5 mW/cm^2. When the diffraction efficiency of the hologram reached the maximum value, the writing beams were blocked, the hologram was kept in the dark and then the photopolymer hologram could be enhanced automatically. Since our PQ:PMMA photopolymer is not sensitive to the red laser beam, the whole process of the grating formation can be monitored in real-time by use of a weak 632.8-nm He-Ne-laser beam at Bragg-matched angle. The resulting curve is shown in figure 6. It is seen that in the writing region (region (I)), the diffraction efficiency quickly reaches the maximum of 12% for the exposure time of ~200 seconds and then it begins to drop for further exposure. In the region (II), the writing beams are blocked and the diffraction efficiency continues to increase. The maximum enhancement can be obtained as high as ~70% of the diffraction efficiency after standing in the dark for 3-4 hours. At room temperature, the enhancement induced by the diffusion of the MMA and PQ molecules seems to be permanent; the refractive index modulation of the post-treated hologram does not change even when we illuminate the hologram by using a strong single 514-nm laser beams. In addition, it is also interesting to see the characteristics of this enhanced hologram under high temperature and with long term reading. Figure 7 shows the experimental results. After the post-enhancement and single-green-light exposure testing, in the region (I), the oven is heated to 50°C. It can be seen that the diffraction efficiency firstly drops very fast due to Bragg mis-matched reading induced by the thermal expansion of the hologram. When we tuned the reading angle of the He-Ne beam back to the Bragg-matched angle and then the diffraction efficiency reaches ~55%. The diffraction efficiency of the hologram keeps rising and reaches ~72% as the hologram is heated for ~2 hours. In the region (II), the temperature of the hologram is return back to room temperature and we also monitor the dynamics of the diffraction efficiency of the hologram. It can be seen that the diffraction efficiency also firstly drops very fast due to Bragg mis-match and then reaches 66% after retuning of the reading angle. Continuing to monitor the diffraction efficiency of the hologram shows the long-term stability of the enhanced hologram. It can be seen that the diffraction efficiency maintains as high as 72% for more than 20 hours. Therefore, we conclude that the dark enhancement of the hologram in PQ:PMMA photopolymer is permanent and can be long-term stable.

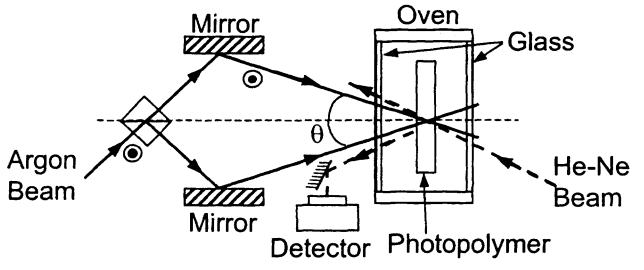

Figure 5. Schematic diagram of the experiment setup to study the dark enhancement.

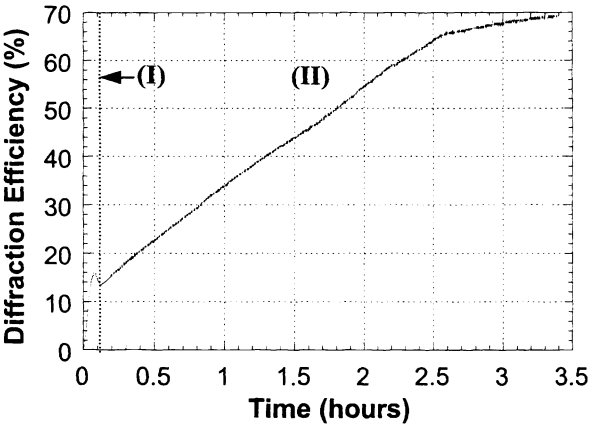

Figure 6. The resulting curve for dark enhancement in 2-mm thick PQ:PMMA photopolymer.

4.2. The temperature effect of the dark enhancement

Dark enhancement, which produces a great increase in the refractive index modulation, has two additional advantages: it produces permanent refractive index changes (hologram fixed automatically), and it produces very little noise. Therefore, the quality of the hologram can be maintained after the enhancement. However, it has a disadvantage: at room temperature, it takes long time (~3-4 hours) to reach the maximum diffraction efficiency. Since we believe that this dark enhancement involves further diffusion of the PQ and MMA molecules after primary recording, the thermal treatment will therefore be helpful to increase the rate of the dark enhancement.

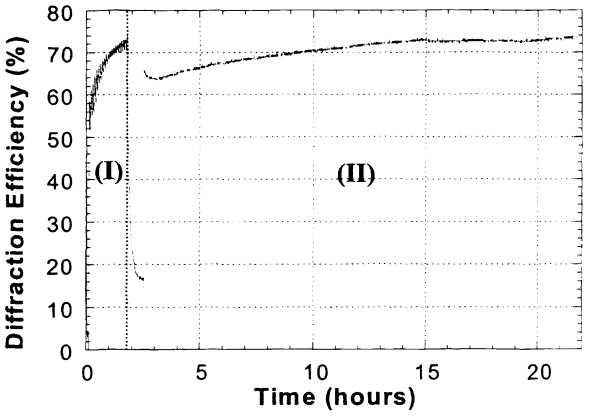

Figure 7. The resulting curve for testing the thermal and long-term stability in 2-mm-thick photopolymer.

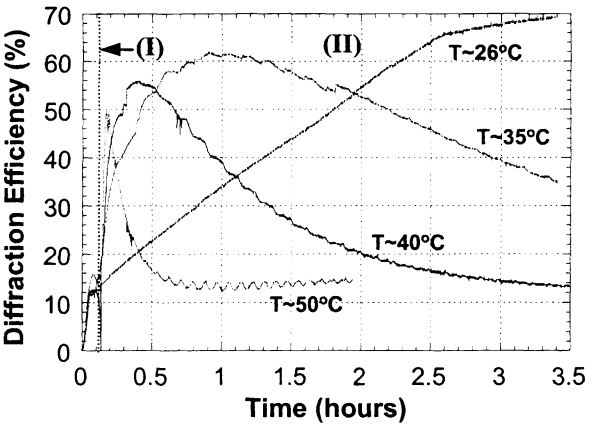

Figure 8. The resulting curve for testing the thermal treatment of the dark enhancement for the different temperatures.

Figure 8 shows the change in diffraction efficiency of the holograms recorded in 1.2-mm-thick PQ:PMMA photopolymer samples under the dark enhancement as a function of both temperature and heating time. Again, in the writing region (region (I)), the temperature of all polymer samples are set at room temperature and the diffraction efficiency of each hologram quickly reaches the maximum of 12% for the exposure time of ~200 seconds. In the region (II), the two writing beams are blocked and the dark enhancement occurs at the different temperature controlled by the oven. It can be seen that the diffraction efficiency firstly increases with heating time, reaches a maximum and then begins to drop for further heating. Also, the rate of change increases with increasing temperature. However, both the maximum and final values decrease with increasing temperature. It can also be seen that the rate of the decay increases with increasing temperature. We believe that this drop effect of the diffraction efficiency might be caused by the diffusion of the large molecules, such as PQ radicals move from the bright region to dark region of the original light interference pattern. The detail mechanism of the dark enhancement under thermal treatment is still not well understood. It needs the further chemical analysis to give more detailed explanations.

5. CONCLUSION

We have presented a method for synthesizing high-optical-quality thick photopolymer for volume holographic data storage. The characteristics of the volume holographic recording have been investigated. We have analyzed the limitation of the diffraction efficiency of single recording due to the scattering noise during optical exposure. A dark enhancement method of the holographic grating using the post-diffusion of the residual monomer molecules has been proposed to increase the diffraction efficiency of a single hologram. Temperature effect of the dark enhancement has also been investigated.

6. ACKNOWLEDGEMENT

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