Influence of fabrication conditions on characteristics of phenanthrenequinone-doped poly(methyl methacrylate) photopolymer for holographic memory

Shiuan Huei Lin [a,*], Sheng-Lung Cho [b], June-Hua Lin [c], Ken Y. Hsu [c], Sien Chi [b,c]

[a] Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan
[b] Department of Electro-Optical Engineering, Yuan Ze University, Chungli 32001, Taiwan
[c] Department of Photonics & Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

ARTICLE INFO

ABSTRACT

In this paper, we experimentally investigate the influence of the fabrication conditions on holographic characteristics in phenanthrenequinone-doped poly(methyl methacrylate) (PQ:PMMA) bulk photopolymer. In our investigation, the PQ:PMMA bulk samples are fabricated by use of a two-step thermo-polymerization method. We firstly propose to monitor relative viscosity of the monomer solution during the sample preparation to obtain a reliable criterion for material fabrication. We then compare experimentally characteristics of 2-mm thick samples fabricated with different conditions for holographic memory. The results show that the conditions in the first step play a important rule for fabricating bulk PQ:PMMA samples with good optical uniformity. In addition, the conditions in the second step play the rule for controlling the concentration of residual monomer and determine holographic characteristics. These results can provide a useful rule for fabricating bulk PQ:PMMA photopolymers for further applications on volume holographic data storage.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Volume holography using thick recording materials is considered as a potential candidate for future 'ultra' storage technologies, because its three-dimensional structure facilitates terabyte (TB) storage capacity and the page oriented format allows one to achieve gigabyte (Gb)s^{-1} data write and read rate. Currently, this technology is on the horizon for commercial applications, but is still rich for research activities [1–4]. Among the various aspects, finding a suitable volume holographic material is one of the most important issues. More recently, the research efforts have been shifted to photopolymer materials, because their fabrication is less involved and costly. Modifying the material components and fabrication procedures to fit into requirements of different applications is simpler [5–10]. However, in the most photopolymer materials, the modulation of the index of refraction for holographic recording is caused by photochemical polymerization, which often unavoidably causes significant local variation of the volume and consequently induces a strong material shrinkage during holographic recording. It leads to a loss of Bragg condition of readout beam such that the recorded information cannot be read out completely [10]. This phenomenon becomes more severe as the material thickness is increased for achieving larger storage capacity. Thus, one of the fundamental keys for material development is the availability of low photo-induced shrinkage property.

Recently, a kind of diffusion amplification photopolymer material, named as PQ:PMMA which is a composite of phenanthrenequinone-doped poly(methyl methacrylate) has been shown to be a promising candidate for alleviating the shrinkage problem [11–18]. The doped elements in these materials are used for recording holograms, instead of the photoinduced polymerization or crosslinking mechanism. The polymerization of monomers in these materials is only used to make a strong polymer matrix for supporting thickness and optical quality of medium. The mechanism for recording hologram in PQ/PMMA is produced by the photochemical reactions involved with photosensitive elements; in this case PQ as well as residual monomers, MMA and polymer chain, PMMA. Hence, the key to achieve this goal lies in the material fabrication conditions to control the concentration of the residual monomer for photoreaction elements. It has been successfully demonstrated to fabricate few-mm-thick PQ/PMMA photopolymers by use of a two-step thermo-polymerization technique. The experiments show that the samples have indeed ultralow shrinkage and refractive index change comparable to other photopolymer materials [15–18]. However, the precise influence of the fabrication conditions in each step to the optical and holographic

---

* Corresponding author.
E-mail address: lin@cc.nctu.edu.tw (S.H. Lin).

characteristics of the samples has yet to be unambiguously established. In this paper, we present experimentally influence of preparation conditions to the PQ:PMMA photopolymer samples. We first present how the fabrication conditions in the first step affect the optical quality of bulk sample and propose a criterion to choose the conditions by measuring the relative viscosity of the monomer solution during the sample preparation. We then characterize PQ:PMMA samples prepared with different fabrication conditions to identify the key factors of determining the characteristics of the samples for holographic memory. These two experimental results provide a useful rule for determining fabrication conditions and optimizing characteristics of thick PQ:PMMA samples for volume holographic memory.

2. The fabrication of thick PQ:PMMA photopolymer samples

Our two-step thermo-polymerization to fabricate bulk PQ:PMMA samples usually starts with raw materials: liquid monomer MMA, photo-sensitizer PQ, and thermo-initiator AIBN (2,2-Azo-bisisobutyrolnitrile). In the first step, the thermo-initiator AIBN ($\sim$ upto 2.0 wt. %) and PQ molecules ($\sim$ 0.7 wt%) are dissolved in solvent MMA. The solution is stirred (using a magneto stirrer) in a glass bottle at certain temperature (hereafter, named as stirring temperature) for a certain period (stirring time) until it becomes homogeneously viscoid. In the second step, the viscoid solution is injected into a glass mold, and then put it in an oven which is kept at higher temperature (baking temperature) to accelerate the polymerization process. After certain period (baking time), the sample become a self-sustained solid block, and can be removed from the mold for optical testing and holographic applications without post processing.

In experiments, we found that these two steps are necessary to fabricate samples with good optical quality. The purpose of first step is to dissipate N_2 gas from the thermo-decomposition of AIBN and huge amount of heat from radical generation of MMA monomers during the initial stage of thermo-polymerization of MMA. When they are released completely from the MMA solution, bubble-free bulk sample can be fabricated so that optical quality of the sample can be good enough for experiments. Thus, in the first fabrication step the solution was stirred (using a magneto stirrer) in a glass bottle at low temperature one could ideally obtain a sticky solution with clear phase. This sticky solution is injected into a glass mold to form a self-sustainable bubble-free block in the second step. To confirm these descriptions, we fabricated two samples using different stirring time at 30 °C in the first step and baking time of 5 days at 45 °C in the second step. The pictures of the final polymer samples are shown in Fig. 1. It is seen that the PQ:PMMA polymer bulk in the right bottle, which was stirred for 16 h has clear phase and uniform transparency. The bulk in the left bottle, which had not proceeded in the first step (zero-h stirring) seems to deliver a very distorted shape with unacceptable optical quality. Concerning these points, it is obvious how to choose the timing to possess molding in the second step plays a critical rule for our two-step method.

One can observe that the liquid solution becomes thicker and thicker as a result of the polymerization of liquid MMA initiated by AIBN. Thus, the viscosity of the solution is a good indicator for choosing timing under different temperature. For the experimental confirmation, we fixed the stirring temperature at 30 °C and used the stirring time as parameter to determine timing. A quantitative relationship between the viscosity of the MMA solution and stirring time, t_s is measured. It can be performed by an Ubbelohde capillary (as illustrated in Fig. 2 (a)) bathed in 30 °C water. In experiments, γ hole was sealed and the MMA solution was injected to the bottom vessel through α hole until the surface
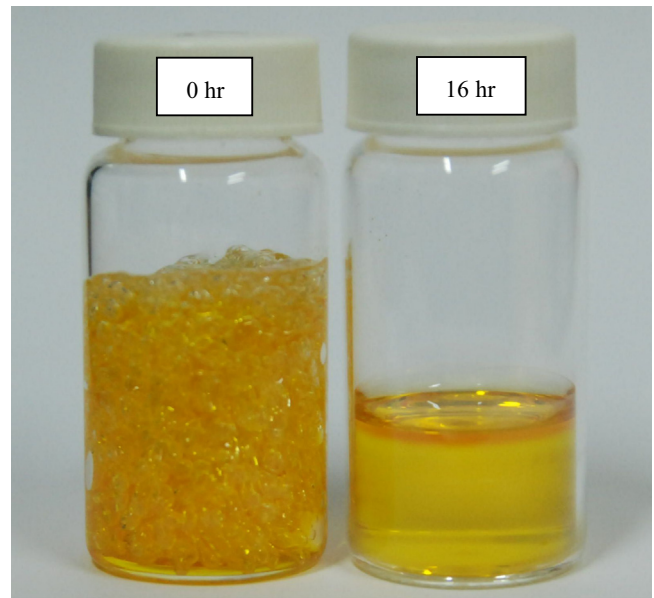

Fig. 1. The pictures of the PQ/PMMA polymer in the sample bottle with different first step stirring time 16 h and 0 h.

of the solution was over A line. The β hole and the z side of the vacuum suction were then connected. The solution was draw to vessel on right-hand side by the suction until the surface of solution was over B line. When the y side was turn on to depress suction, the surface of solution was falling because of the gravity and the falling time from B to C line was measured. In a linear approximation, the falling time is proportional to the viscosity of the liquid. The relative viscosity can be expressed as: $\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$, where η, ρ, and t represent viscosity, density, and falling time of sample solution under different string time, respectively, and η_0, ρ_0, and t_0 represents the corresponding parameters of a reference liquid. In our case, it is the MMA solvent. By measuring the falling time of the sample and MMA solutions, the relative viscosity of the solution under different string time can be determined assuming that the density ρ and ρ_0 are the same during material preparation. The experimental results of viscosity measurement are summarized and plotted in Fig. 2(b). It is seen that when the stirring time is less than 16 h, the relative viscosity remains a small value, further increases rapidly. This result implies that polymerization is speeding up due to propagation of polymer chain after 16 h. By eye visual, it was seen that the solution started to become sticky. In addition, in experiments, we found that when the stirring time is longer than 16 h, the baking temperature and time in the second step were not critical issues to obtain bulk PQ:PMMA sample with good optical quality, as long as the baking temperature is much less than the boiling temperature of MMA solution ($\sim$ 110 °C). Furthermore, when the stirring time is over 24 h, the solution becomes too sticky to take the solution out of the glass bottle. Thus, it concludes that the timing to reach at high growing rate of the relative viscosity, which represents high thermo-polymerization rate, can be chosen to proceed the second step for molding samples. At 30 °C, the period between 16 h and 24 h which produces the relative viscosity of solution in the range of $\eta_r = 10 \sim 110$ is acceptable.

On the other hand, this acceptable relative viscosity can be used as a criterion to determine timing when the stirring temperature is changed. For a chemical reaction, the relation between the speed of reaction and experimental conditions can usually be determined by using Arrhenius equation [22,23]. Thus, for our case, the temperature dependence of the stirring time, t_s to