Diffraction Gratings of Photopolymers Composed of Polyvinylalcohol or Polyvinylacetate Binder

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Abstract: Holographic gratings in two kinds of photopolymers (PPs) were fabricated by optical interference method. Polyvinylalcohol (PVA) and polyvinylacetate (PVAc) were employed as polymer binders and photopolymerization of acrylamide (AA) was confirmed using infrared spectroscopy. Dynamic behavior of the diffraction efficiency was monitored and its temporal stability at room temperature was also observed. Additionally, the temperature dependence of these gratings was investigated in two PPs. The surface topographical change of the photopolymer layer was observed by atomic force microscope (AFM).

Keywords: photopolymer, holographic grating, diffraction efficiency, temperature dependence.

Introduction

Organic photopolymers (PPs) have significant advantages over other kinds of photofunctional materials prepared by emulsions, such as dichromated gelatin and silver halides, which will have important applications in holographic data storage and other fields.[1-7] Therefore, research interests about development of new organic PP have been increased in this field recently.[8-13]

During holographic recording, the film sample is placed within an interference pattern formed by the intersection of two coherent laser beams. The interference pattern consists of a periodic variation of bright and dark fringes due to the constructive and destructive mode. In general, the PP consists of polymeric binders, vinyl or acrylic monomers, photoinitiator system, crosslinker, and sensitizing dyes.[14,15] The host binder act as a supporting matrix containing the other additive components. The monomers serve as the governing species to control the index modulation, induced by optical interference. When the PP contains high concentration of low molecular weight compounds in the matrix, we cannot avoid crystallization and phase separation to induce optical opaqueness of the film. Although the plasticizing effect from those additives can be expected to facilitate the diffusion of the monomer, it is not advantageous for the film forming and the optical properties.

First of all, the incident light is absorbed by the photoinitiator system to produce free radicals that result in active radicals and intermediate. Then, monomers will be diminished in the bright regions and causes a concentration gradient, which then induces monomer diffusion from the unexposed dark region.[16,17] Finally, termination of radical propagation occurs by recombination. The refractive index modulation arises from the density and compositional differences of the molecular chains in the adjacent two regions.

In this paper, we monitored the dynamic grating formation in two kinds of PPs by real-time optical recording. Photopolymerization of acrylamide was confirmed by infrared spectroscopy in the presence of visible light sensitive initiator. Temporal stability of the diffraction efficiency at room temperature and the temperature dependent characteristics of these gratings were investigated in two PPs. The surface topographical change of PP film was also investigated by atomic force microscope(AFM).

Experimental

Sample Preparation. We selected polyvinylalcohol (PVA) and polyvinylacetate (PVAc) as the binders for photopolymer-1 (PP-1) and photopolymer-2 (PP-2), respectively. All the other chemicals used for the preparation of the PP film samples are acrylamide (AA), *N,N*-methylenebisacrylamide (BAA), triethanolamine (TEA), and yellow EOSIN. The

solvents were deionized water and dried methanol for PVA and PVAc, respectively. The chemicals used for the preparation of the PP film were purchased from Aldrich Chemical Company, used without further purifications. We removed a trace of inhibitor in the commercial monomers such as AA and BAA. The solution was cast onto the leveled glass substrate and dried at room temperature in dark room for at least 48-72 h. The weight composition of all components is selected as follows: Polymer binder: AA: BAA: TEA: EOSIN Y = 1.0:0.6:0.07:0.4:0.01.

Optical Setup for Holographic Grating Recording. The schematic diagram for recording the gratings and measuring the diffraction efficiency is illustrated in Figure 1. The Argon ion laser ($\lambda = 488$ nm) is used in recording and the He-Ne laser (p-polarized, 632.8 nm) is used to probe the recorded grating. Two vertically plane polarized (s- & s-) 488 nm light beams with equal intensity are obtained by adjusting the quarter wave plate and the polarizers appropriately, which is used for fabricating the holographic grating. The He-Ne probing laser is horizontally (p-) polarized. The angle (2θ) between the interferential beams is approximately 14.6°, so we can get the grating period of 1.92 μm determined theoretically.

The temporal growth of the first-order diffracted light intensity can be monitored in real-time with a probe light from a He-Ne laser, which is incident at Bragg angle. The first-order diffracted light from the sample is monitored by a silicon detector during the exposure of the excitation beam. The signal from a mechanical chopper is input to a lock-in amplifier as a reference signal. Even though the PP is insensitive to the He-Ne laser, the intensity of the probe beam is maintained lower than 1 mW/cm² in order to minimize its
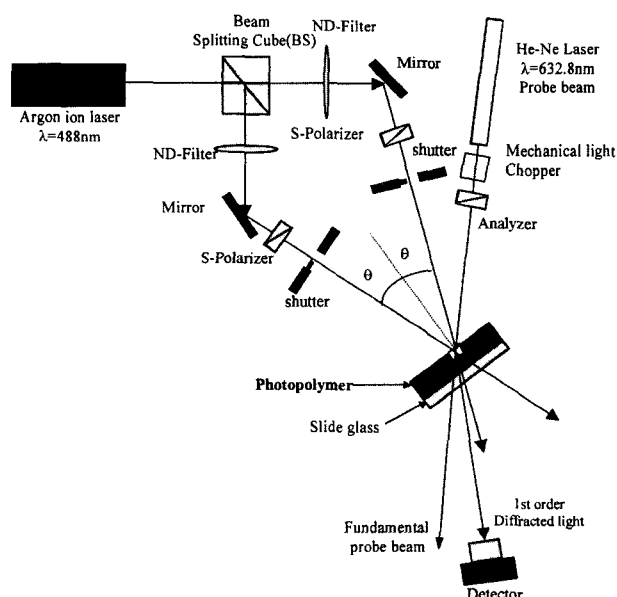
influence on the photopolymerization. The sample was mounted on the holder with one slit and several holes on it. The sample can be put into the holder through the slit. One hole is used for monitoring the diffracted light and one another hole is used for probing the temperature. All the experiments are performed dark room at room temperature.

Results and Discussion

Diffraction Behavior of Photopolymer-1 (PP-1). We prepared PP-1 using PVA binder with the other additive components. This PP was already known and their properties were reported in the literature.[15,18] All samples used in this study contain the same concentration of the monomer, the crosslinker, the photoinitiator, and the photosenstizer. Also, polymerization of the monomer was performed following the radical photopolymerization method. The photoinitiation could be performed by mixture of TEA and EOSIN Y. In this case the molecular weight of PVA was selected around 13,000-30,000. Low molecular weight improves the solubility of PVA in water. The other composition of the low molar mass compound was optimized to prevent from phase separation and severe crystallization after drying the film samples.

We observed the infrared (IR) spectra of the samples before and after visible ($\lambda = 488$ nm) light irradiation in order to confirm the progress of radical polymerization of AA (Figure 2). According to the IR spectral change, we could figure out that AA monomers were polymerized well under this irradiation condition. The double bond stretching band of AA appeared at 1607 cm⁻¹ before the visible light irradiation (Figure 2(a)) and its absorbance decreased significantly accompanying with the other combination bands after irradiation (Figure 2(b)). This indicates that AA underwent the polymerization under irradiation of the visible light. This spectroscopic study helped to optimize the irradiation time for saturation of the diffraction efficiency, indicated by the

Figure 1. Experimental setup for measuring the diffraction efficiency.
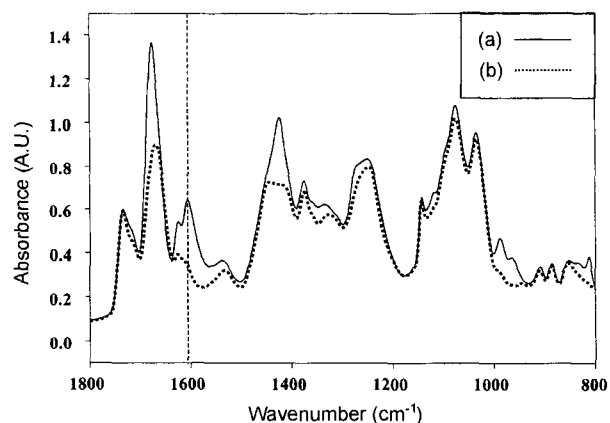
Figure 2. Infrared spectra of PP-1: (a) before visible light irradiation; (b) after visible light irradiation.

stabilization of the absorbance at 1607 cm⁻¹.

We studied the diffraction properties of the PP-1 under different exposure intensities to estimate the light sensitivity. Figure 3 shows the dynamic behaviors of the diffraction efficiency under different exposure intensities. It is clear that the diffraction efficiency increases with the increase of the exposure intensity. However, the diffraction efficiency of this kind of grating mainly depends on the polarization states of the recording beams, the exposure intensities, the degree of polymerization,[19] the thickness of the film sample. There is a slight decrement in diffraction efficiency for prolonged irradiation of the excitation beams, which is a similar result in the literature.[8] Also as the intensity is higher, the decrement is larger. The reasons why the diffraction efficiency decreases after saturation of exposure might be due to the cross-talk of the holographic grating. Additionally, the rate of monomer diffusion becomes higher and the polymerization goes further at higher intensity so that the larger volume shrinkage on the localized area may occur consequentially.[20] Therefore, we could observe a small extent of decrement of the diffraction efficiency. It is believed that there is optimal exposure intensity for the PP, which will be reported elsewhere.

Diffraction Behavior of Photopolymer-2 (PP-2). We prepared PP-2 using PVAc binder with the same additive components and concentration used before. In this case, the molecular weight of PVAc was selected around 80,000. It shows good solubility in absolute methanol. In this formula, we used 2',4',5',7'-tetrabromofluorescein obtained after titrating EOSIN Y with hydrochloric acid and the product is well-soluble in alcohol.

The other composition of the low molar mass compound was identical with that in the previous sample (PP-1). We also recorded the infrared spectra of the samples before and after visible light irradiation in order to confirm the progress of radical polymerization of AA (Figure 4). In this case we

used methanol as a solvent and we assumed very little residual solvent inside the sample after long-term drying process. Although the plasticizing effect from residual solvent is weaker than the previous PVA sample, PVAc (T_g~32 °C) has much lower glass transition temperature than PVA (T_g~85 °C).

According to the spectral change, the double bond stretching band of AA at 1606 cm⁻¹ decreased in the same fashion we observed in the previous sample (PP-1) accompanying with the other harmonic bands. This indicates that AA in PVAc also underwent the polymerization under irradiation of the visible light. We also studied the variation of the diffraction efficiency under different exposure intensities to estimate the light sensitivity. Figure 5 shows the dynamic behavior of the diffraction efficiency under different light intensities. It is clear that the diffraction efficiency increases with the increase of the exposure intensities although the rising rate has some discrepancy to the increasing order. This experiment was performed under identical exposure
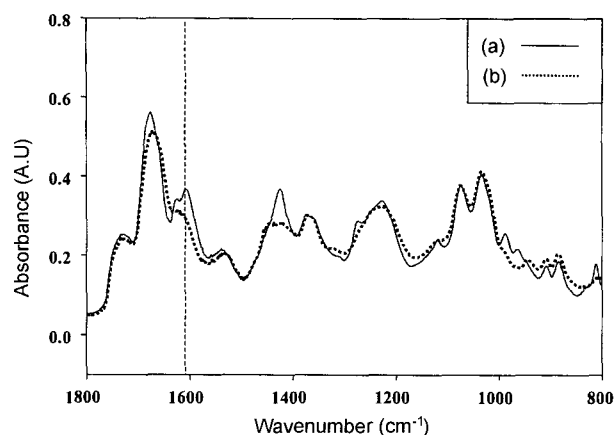
Figure 4. Infrared spectra of PP-2: (a) before visible light irradiation; (b) after visible light irradiation.
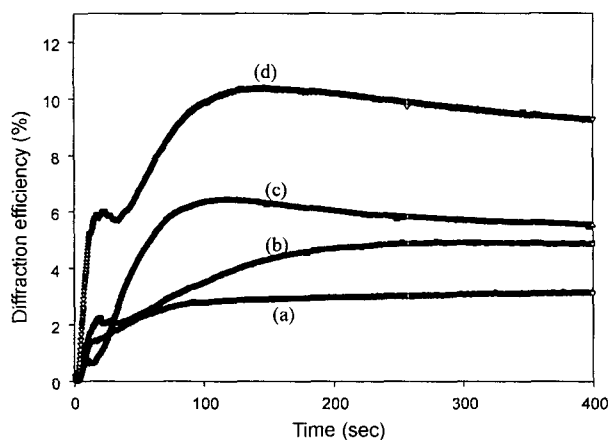
Figure 3. Diffraction efficiency of PP-1 with the change of the light intensity: (a) 3.54; (b) 7.08; (c) 14.16; (d) 28.32 mW/cm².
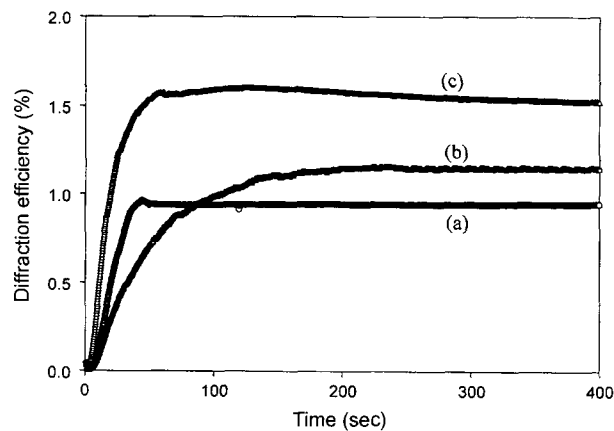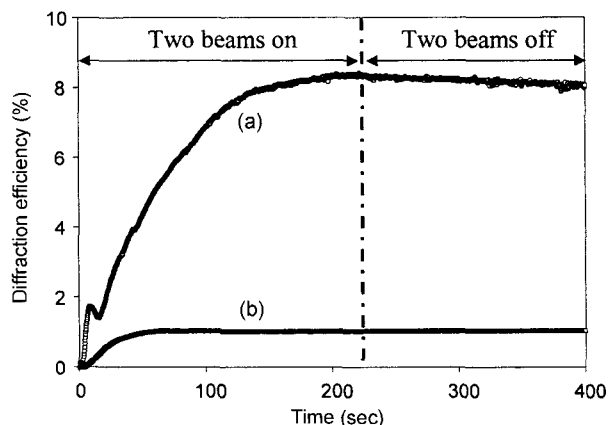

Figure 5. Diffraction efficiency of PP-2 with the change of the light intensity: (a) 7.08; (b) 14.16; (c) 28.32 mW/cm².

dose used in the previous sample. Compared to PP-1, this sample does not show that high diffraction efficiency. It can be conjectured that the polymerized chains of AA have some degree of freedom to be mobile inside the matrix since the glass transition temperature of polymer binder is inherently very low ($\sim 32\,°C$). Then, after adding the all additives, the T_g will become much lower than that of PVAc. In the presence of temperature rise from the pumping light source, the molecular chains will have much degree of freedom. According to above reason, the surface relief structure will not be well defined, which will be described in the last section. In this case we could not observe the similar decreasing behavior over a prolonged irradiation. This means that degree of polymerization in the bright region is not as high as that in the previous PP-1 sample. However, at higher intensity, we also can observe the slight decrement just like we did in PP-1 sample, which is relatively very small.

We measured the change of the diffraction efficiency after blocking two pump beams. We block the pump beams after saturation of the diffraction efficiency. PP-1 shows much higher diffraction efficiency than PP-2 and however, at prolonged irradiation of visible light, slight decrement was observed in PP-1 (Figure 6). This may be attributed to the backward migration of polymer chain from bright to dark region in part. In PP-2, the decrement of diffraction efficiency is negligible. Inherently, the diffused amount of monomer was relatively very small so that the reduction of the refractive index cannot be detected significantly. Resultantly, two PPs were evaluated to be fairly good in term of the temporal stability at room temperature.
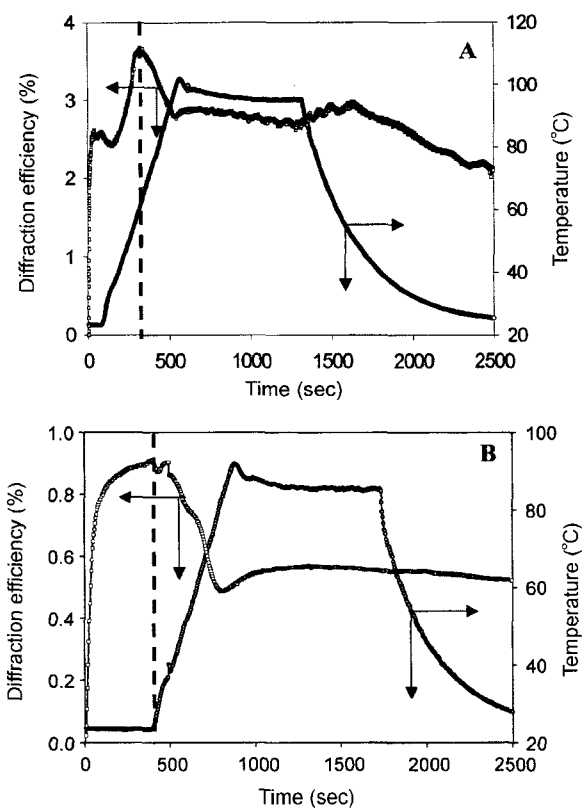
Temperature Dependence of the Saturated Diffracted Light Intensity. The general process of producing holograms in conventional PP involves three steps: (1) holographic exposure, (2) UV irradiation, (3) heat treatment. During the heat treatment, the refractive index modulation and hence the efficiency will change. The polymerized molecular chains can migrate from bright to dark region in some degrees due
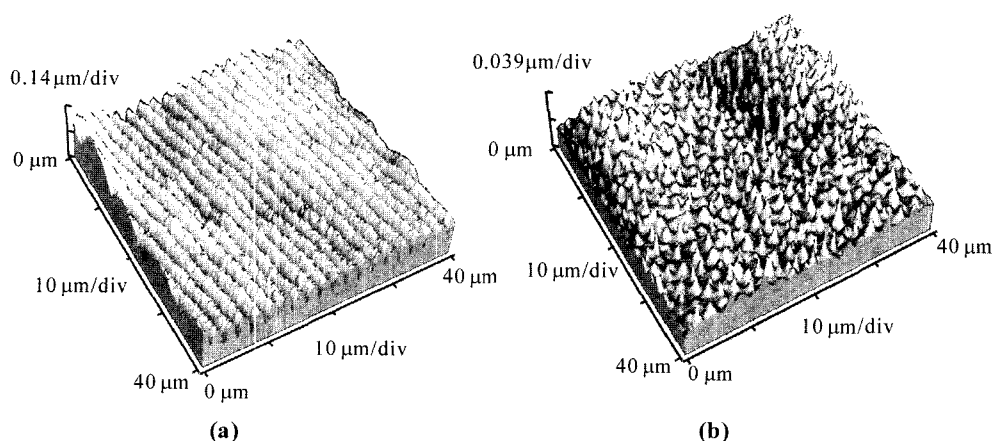
to low glass transition temperature of the PP. The rate of diffusion of monomer will be enhanced during raising the temperature.

We recorded the change of the temperature of the sample spot during heating the sample. When the diffraction efficiency of the grating reaches its maximum value and becomes stable, we block the pump beams and start to heat the sample. Figure 7 shows the dynamic development of the grating with the change of temperature, (A) is for PP-1 and (B) for PP-2. The exposure intensity for both samples is 7.08 mW/cm^2. It is easy to analyze the change if we divide all the time into three stages according to the temperature range, namely, (1) the heating stage, (2) the isothermal stage, and (3) the cooling stage. In the case of PP-1, we could observe the increasing behavior of the diffraction efficiency from room temperature to 60 °C. In this range, we thought that the polymerized AA chains become unstrained and the density of the hydrogen bond will increase for stabilization of the chain molecules in a new geometry. Then the diffraction efficiency fell down to the initial saturated value due to the molecular chain migration. Contrary to this sample, PP-2 showed poor stability with the temperature. When starting to increase the temperature from the room temperature, the diffraction efficiency starts to decrease and stabilize to a certain level that is much lower than the initial saturated diffraction

Figure 6. Temporal stability of the diffraction efficiency without pumping beams: (a) PP-1; (b) PP-2.

Figure 7. Temperature dependence of the saturated diffraction efficiency: (A) PP-1; (B) PP-2.

Figure 8. Atomic force micrographs of PP-1 and PP-2: (a) PP-1; (b) PP-2.

efficiency value. This is wholly attributed to a low glass transition temperature of the PVAc binder and the polymerized AA chains displaced randomly to disrupt the period grating structure. This will induce the diminishment of the grating structure on the film surface that can be observed in AFM picture.

Atomic Force Micrographs of the Surface of Photopolymers. Finally, we observed the surface of the film after recording the holographic grating by AFM. AFM images of the PP-1 and PP-2 were taken after recording the grating and storing them at room temperature for 2-3 h as shown in Figure 8. The exposure intensity is 14.16 mW/cm² for two PP films. The depth of modulation for PP-1 is 120.6 nm and the period of the grating is 2.10 μm. The theoretical value for the period of the grating is 1.92 μm, so the experimental periodicity of the grating fits well to the theoretical one. It is obvious that our PP-1 has relatively deep modulation depth compared to the conventional PP. However, as is told previously, in the case of PP-2, the relief grating structure was not clearly observed. The grating structure arising from large mass transport was diminished after 2-3 h at room temperature. Due to the polarization states (s- & s-) of the two-pump beams, the pumping light will induce pure intensity interference. We now are making much effort to study different kinds of modulation grating with the polarization states of the pumping light using the new PPs.

Conclusions

The diffraction holographic grating is recorded by optical interference method successfully. The dynamic holographic recording characteristics of the two PP systems have been studied with the change of the pumping beam intensity. With the increase of the exposure intensity in a certain range, the diffraction efficiency will increase accordingly. However, we could figure out the optimum dose of exposure for achieving the maximum and stable diffraction efficiency.

The temperature dependence of the holographic grating was also studied, which have important property in the practical application of the grating under high temperature circumstance. Finally, we made a clue to design and formulate the highly functional PP that can show better environmental stability. Particularly, thermal stability will be enhanced by selection of the proper polymer matrix whose glass transition temperature is reasonably high. We also have to consider the inter- and intra-molecular interaction between the polymer binder and the newly formed polymer for achieving the good performance of photopolymer.

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