THE INVESTIGATION OF VOLUME CHANGE OF PHOTOPOLYMERIZATION BY HOLOGRAPHY

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The volume of a photopolymerizable medium may be changed after monomer is converted into polymer. One has not yet precise method for measuring a volume change when a photopolymerization reaction occurs in a film. This paper proposes a holographic method for measuring the volume change (that is the thickness change) of a photopolymerizable film. The method relies on the fact that the volume change can cause a holographic grating period change and result in peak replay wavelength shifts. The volume change can be obtained from the Bragg law, compared the experimental result with the theoretical calculated value.

1. Introduction

Holography is most widely used in a three dimensional display, a holographic interferometry, a holographic nondestructive testing, a holographic optical element and so on. But holography can also be used as a powerful tool for the investigation of a variety of photochemical and photophysical processes[1]. These experimental techniques rely on the fact that small spatial modulation of material optical properties can deflect an incident light beam into another direction. By following the growth or decay in intensity of this deflect beam, one can follow the underlying photochemical and photophysical process producing the changes in optical properties. F. W. Deeg [2] and R. K. Grygier [3] evaluated the photochemical quantum yields by holography. D. M. Burland [4] determined the quantum yields and measured the polymer chain lengths. C. H. Wang [5] investigated the diffusion of small solute molecules in the polymer matrix. During studying new holographic recording materials, we found that volume change of photopolymerization could be measured by holography.
2. Holographic Method for Measuring Volume Change

The volume of a photopolymerizable medium may be changed after monomer is converted into polymer. A volume change can be easily measured by a dilatometer when a photopolymerization reaction occurs in liquid. One has not yet precise method for measuring a volume change when a photopolymerization reaction occurs in a film. We found that a volume change could be measured by holographic method. The method relies on the fact that the volume change can cause a holographic grating period change and result in peak replay wavelength shifts. The volume change can be obtained according to the coupled wave theory [6].

The coupled wave theory assumes that there are only two waves present in the grating: the illuminating wave C and the diffracted signal wave S. It is assumed that the Bragg condition is approximately satisfied by these two waves and that all other orders strongly violate the Bragg condition and hence are not present.

Fig. 1 defines the grating assumed by Kogelnik. The Z-axis is perpendicular to the surfaces of the medium, the X-axis is in the plane of incidence and parallel to the medium boundaries, and the Y-axis is perpendicular to the page. The fringe planes are oriented perpendicularly to the plane of incidence and slanted respect to the medium boundaries at an angle . The grating vector \( \mathbf{K} \) is oriented perpendicularly to the fringe planes and \( |\mathbf{K}| = \frac{2\pi}{\Lambda} \), where \( \Lambda \) is the period of the grating. The angle of incidence for the illuminating wave C in the medium is \( \theta \). The Bragg angle is \( \theta_B \).

![Fig. 1. Notation used to define a thick grating](image)

When the Bragg condition is satisfied we have

\[
\cos(\Phi - \theta_B) = \frac{K}{2\beta}
\]

where
we can write the Bragg law as follow

\[ 2n \Delta \cos \theta_b = \lambda \]

where \( n \) is the average value of the index, \( \theta_b \) is the Bragg angle, \( \Delta \) is the period of the grating and \( \lambda \) is the free space wavelength.

If a recording laser light with wavelength \( \lambda_r \) is split into two beams of equal intensity. The two beam enter the recording medium with the incidence angle \( \theta_0 \), which the average index of the medium is \( n \), then, \( \Lambda_r \), the grating period formed in the medium is satisfied the following equation

\[ 2n \Lambda_r \cos \theta_0 = \lambda_r \]  

the grating period \( \Lambda_r \) can be calculated when the recording wavelength \( \Lambda_r \), the incidence angle \( \theta_0 \), and refractive index \( n \) of the medium are given. The grating period \( \Lambda \) of the experimental value will be equal to that \( \Lambda_r \) of the calculated value and the peak replay wavelength \( \lambda \) will be the same as the recording wavelength \( \lambda_r \) as a result of no volume change of the recording medium after photopolymerization. The incidence angle \( \theta_0 \) of the reconstructing beam is assumed to be equal to the incidence angle \( \theta_b \) of the recording beam. The grating period of the experimental value will reduce and peak replay wavelength will blue shift as a result of shrinkage of the recording medium after photopolymerization. The grating period will increase and peak replay wavelength will red shift as a result of swelling of the recording medium.

From (2) and (3), we have

\[ \Lambda - \Lambda_r = \frac{\lambda}{2n \cos \theta_0} - \frac{\lambda_r}{2n \cos \theta_r} \]

where \( \theta_0 = \theta_b \),

thus the above equation can be rewritten

\[ \Lambda - \Lambda_r = \frac{1}{2n \cos \theta_r} (\lambda - \lambda_r) \]  

The volume change can be obtained from the equation (4), compared the experimental value \( \Lambda \) with the theoretical calculated value \( \Lambda_r \).

3. Experiment

Holographic Setup

The experimental setup is shown in Fig. 2. The grating is created with an argon ion laser
(488nm). The writing light is split into two beams of equal intensity. In a process for forming a reflection grating wherein a reference beam of coherent actinic radiation and an object beam of the same coherent actinic radiation enter a layer of recording medium from opposite side to create an interference pattern in the medium that forms the grating. A system of adjustable mirrors allows the beams to interfere with equal path lengths.

Sample Preparation

The photosensitive coating solution is composed of 0.2g of diethylene glycol diacrylate; 14g of chlorobenzene; 1.2g of methacrylic acid benzyl ester; 12g of polyvinyl acetate solution (25% of polyvinyl acetate, 75% of methanol); 0.6g of N-vinyl carbazole; 0.1g of 3-mercapto-4-methyl-4H-1,2,4-triazole; 0.2g of 2,2'-Bis(0-chlorophenyl) 4,4',5,5'-tetraphenyl-1,2-bilimidazole; 0.005g of sensitizer Dyel (synthesised by ourself). The photosensitive solution is coated onto glass plates, then the coated plates are placed on a platform and formed into a film with a desired thickness on the substrates.

Exposure

Exposure is made with an argon ion laser (488nm). Two light beams from the laser are introduced onto the sensitive material layer as shown in Fig. 2.

4. Results and Discussion

The holographic gratings were constructed by interfering two laser beams at 0° (θ = 0), using the 488nm line (λ) of an argon ion laser. A diagram of the apparatus is shown in Fig. 2.
After coherent exposure, a uniform noncoherent light illumination was used to complete the photopolymerization for fixing. The peak replay wavelength was determined from absorption spectra recorded with a spectrophotometer. The experimental result showed that the peak replay wavelength $\lambda$ was equal to 477 nm. The difference of the peak replay wavelength between $\lambda$ and $\lambda_e$ is

$$\Delta\lambda = \lambda - \lambda_e = -11\text{nm}$$

thus, the experimental peak replay wave length is shorter than the recording wave length ($\lambda_e$).

In our case $n=1.50$,

so that

$$\Delta\Delta = \frac{1}{2n}\Delta\lambda = -3.7\text{nm}$$

From this result it is evident that the volume of the recording medium shrunk after photopolymerization.

As above state, the volume change of the photopolymerizable medium can be easily observed. After interefering and fixing exposure, the peak replay wavelength can be measured with a spectrophotometer. The volume of the medium shrinks if the peak replay wavelength shifts to shorter wavelength. The volume of the medium swells if the peak replay wavelength shifts to longer wavelength.

5. Conclusions

The volume change of a photopolymerizable material can be easily obtained by holography. This method provides a way for designing composition of materials. In some case no volume change materials are required. For example, holographic materials are used for making optical elements. With the method, one may determine which material shrinks and which material swells after photopolymerization, then combine with the two ingredients to get rid of volume change.

Reference