PHOTOPOLYMER MATERIALS FOR
HOLOGRAPHY

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Holography with a blue sensitive photopolymer system and novel repolymerizing fixing methods are described. The photosensitive medium is composed of photosensitizing dye, chain transfer agent, initiator, monomer and polymeric film-forming binder. Coatings are cast from solution onto a washed glass plate.

1. Introduction

Holographic recording materials can be classified into two types, that is, silver halide and non-silver halide. A silver halide plate has a high sensitivity but it has a low diffraction efficiency. This problem limits the applicability of silver halide system. In order to improve the brightness of a reconstruction image, bleaching method and dilute developing method have been adopted, but the diffraction efficiency is not over and above 40%. Thus, phase recording materials have been developed. Dichromated gelatin plate (DCG) is one of high quality non-silver halide plates. A significant advantage of DCG is its high diffraction efficiency (80-90%). The drawback of DCG is its low sensitivity, less several orders as compared with silver halide. Photopolymer systems have promised both high diffraction efficiency and sensitivity. In several publication some characteristics of an earlier experimental holographic photopolymer made by E. I. duPont de Nemours and Company (1), Polaroid Corporation (2), Canon Corporation (3), have been described. The blue sensitive photopolymer materials have a high sensitivity, a high diffraction efficiency, a simple process of making plates. The availability of reliable, an argon ion laser has been used in the photopolymer systems. Thus, the system is an ideal holographic recording material.
2. Experimental

Holographic Setup

The experimental setup is shown in Figure 1. The hologram 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 hologram 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 hologram. 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(−chlorophenyl) 4,4',5,5'-tetraphenyl-1,2-bilimidazole (O-cl-HABI); 0.005g of sensitizer Dye1 (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.

Recording Hologram

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. 1.

3. Results and Discussion

In order to convert monomer into polymer, two conditions are required. One is a eligible monomer, the other is a suitable initiator. Ethylenically unsaturated carbazole monomers and acrylic
monomers have been selected as monomers.

Photoinitiator system used in the study contains a photoinitiator and a sensitizer which extends the spectral sensitivity to blue light region. When the photosensitive medium is irradiated with an argon ion laser light beam, the photosensitizing Dye I absorbs the light and is activated to at least one excited state, then transfers its energy to initiator, o-cl-HABI. The excited o-cl-HABI molecule dissociates into two imidazole radicals which oxidize the chain transfer agents, 3-mercaptop-4-methyl-4H-1, 2, 4-triazole, to generate the free radical for initiating polymerization of the monomers.

In our work crosslinking monomer has been added to improve the image quality and physical properties of the photopolymer. The refractive index modulation has been also enhanced.

In general, what is recorded in the recording medium is the interference pattern that results from the interaction of the reference beam and object beam impinging on the medium. This initial exposure causes polymerization of a part of the monomers, with the amount of polymerization being a function of the intensity of illumination. As the monomer level is depleted by polymerization, fresh monomer diffuses in from neighboring dark regions, thus, setting up monomer concentration and density gradients. The resulting nonuniform polymer distribution yields refractive index variations. After coherent exposure, a uniform noncoherent or coherent light illumination is used to complete the photopolymerization. The holographic image formed in the medium is not destroyed by subsequent uniform actinic exposure, but rather is fixed or enhanced. The index modulation can also be significant enhanced by simply heating the hologram in a conventional oven. The preferred heating time is 60 minutes at 120°C.

Repolymerizing Fixing Methods

A hologram recorded in the photopolymer medium is a phase hologram. It is an important study to investigate how to display and fix the phase variation. Novel fixing methods have been proposed. Trichromatic filters and pseudocolor holograms can be made with the methods. As well-known, Bragg's law,

\[ 2nd\sin\left(\frac{\theta}{2}\right) = \lambda \]  

where \( n \) is the average refractive index of the recording medium, \( \lambda \) is the wavelength of the probe beam in free space (air), \( \theta \) is the angle within the recording medium between the probe beam and the hologram surface, \( d \) is the grating space. According to the equation (1), when \( \theta \) is given, that is, the observation angle is given, \( \lambda \) shifts to the longer wavelength if \( d \) increases, \( \lambda \) shifts to the shorter wavelength if \( d \) reduces. After heating treatment, the peak reflection wavelength of a hologram blue shifts. The hologram can be immersed in organic liquids that swell the coating, the peak reflection wavelength of the hologram red shifts. However, if the hologram is pulled out from
the organic liquids, the wavelength slowly shifts back to its original value. In order to fix the peak reflection wavelength of a hologram and enhance the refractive index modulation, repolymerizing fixing methods are presented. The repolymerizing fixing methods include a rephotopolymerizing fixing method and a rethermopolymerizing method.

(i) The rephotopolymerizing fixing method

The rephotopolymerizing fixing liquid consists of a monomer, for example, hydroxyethyl acrylate; a photosensitizer, for example, 2-ethylanthraquinone and a solvent, for example, ethylacetate. The fixing liquid is coated onto a hologram that has been heated. In order to make the fixing liquid enter the holographic medium quickly, the hologram can be slightly heated. The hologram may be destroyed if the fixing liquid enters the medium slowly. The hologram is exposed to ultraviolet light as the peak reflection wavelength of the hologram shifts to a wavelength which one requires. The monomer can be converted to polymer. The peak reflection wavelength of the hologram can be fixed.

(ii) The rethermopolymerizing fixing method

The rethermopolymerizing fixing liquid consists of a monomer, for example, hydroxyethyl acrylate; a thermoinitiator, for example, peroxy benzoic amide and a solvent, for example, ethylacetate. The fixing liquid is coated onto a hologram that has been heated. The hologram is placed in an oven as the peak reflection wavelength of the hologram shifts to a wavelength which one requires. The monomer can be converted to polymer. The peak reflection wavelength of the hologram can be fixed.

Applications

(i) Trichromatic filters

Filters play an important role in many fields of scientific techniques. They are widely used in the photography, the film, the microscope, the laser, the optical communication, the biology, the astronomy and so on. Trichromatic holographic filters can be made with stated methods. Three reflection holographic gratings can be evaluated as shown in Fig. 1. under the same condition. After heating treatment, the three reflection holographic gratings can be processed according to the repolymerizing fixing methods. Red, green and blue filter can be obtained respectively.

(ii) Pseudocolor holograms

A color image can be reconstructed by a color hologram. The hologram may be recorded with a white light or a He-Ne laser that emits a red light (633nm) and an argon ion laser that emits a green light (514nm) and a blue light (488nm). A hologram that is recorded with a monocolor laser light can only reconstruct a monocolor image at a given viewer angle. Three holograms can be made with an argon ion laser (488nm) only by stated methods. After heating treatment, the holograms can be processed respectively according to repolymerizing fixing methods. Red, green, blue, three color image can be obtained individually at the same given viewer angle. A pseudocolor image can be
reconstructed by three-in-one combination.

4. **Characterization**

The characterization of the photosensitive medium can be measured in the following ways, that is, sensitivity, diffraction efficiency and resolution.

**Sensitivity**

The sensitivity of the photopolymer materials has ranges of 30 to 300 mJ/cm² with the 488nm beam of an argon ion laser.

**Resolution**

The resolution can be calculated from the equation (1)

\[
d = \frac{\lambda}{2n \sin \left( \frac{\theta}{2} \right)}
\]

where \( n \) is the average refractive index of the recording medium, \( \lambda \) is the wavelength of recording beams in free space (air), \( \theta \) is the angle within the recording medium between the reference beam and the object beam, \( d \) is the grating space. The resolution of materials is over 4000 lines per millimeter.

**Diffraction Efficiency**

Diffraction efficiency (\( \eta \)) is calculated as the ratio of the diffracted probe beam intensity (\( I_d \)) to the incident probe beam intensity (\( I_0 \));

\[
\eta = \frac{I_d}{I_0}
\]

The diffraction efficiency of a hologram depends on exposure, the visibility of the exposure intensity, angle between the reference beam and the object beam, the thickness of the photosensitive layer, the treatment methods and the type of holograms. The diffraction efficiency of a hologram relates also to the measuring ways.

No matter which the measuring ways may be used, the results of our experiment show that the brightness of a reconstruction image of a hologram recorded in the photopolymer material is the same as that recorded in the DCG.

5. **Image Stability**

Many applications of holographic optical elements require stability in a humid, warm environment. The medium is really water proof. Changes in the structure of photopolymer
holograms during environmental testing were studied. After a coherent exposure, a noncoherent uniform fixing exposure and a heating treatment, the hologram was immersed into a water bath. Two days later, the hologram was pulled out from the water bath and dried. No change of the physical properties of the hologram has been observed. Our holograms are stable to natural environmental condition.

6. Conclusions

The photopolymer recording material has a high sensitivity, a high diffraction efficiency and a high resolution. Holograms made with the material are insensitive to humidity and stable to natural environmental condition. In order to enhance the refractive index modulation and fix the phase variation, polymerizing fixing methods have been developed. Trichromatic filters and pseudocolor holograms can be made with the methods.

References

(1) "Du Pont Launches First of New Polymer Holomaterials" Holography News Vol. 4, No. 1, February 1990
