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Stretching the sensitivity and stability of an acrylamide based photopolymer material with mixture of dyes

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ABSTRACT

The limited absorption range of photopolymers in the visible region was always a matter of concern due to their wide-spread application in the field of holography. The present work has investigated the possibility of extending the limited absorption range towards the entire visible range by simple modifications in the photopolymer composition so that panchromaticity can be invoked in the material. Here modification was done on already developed photopolymer material by adding another photosensitizer. Studies showed that holographic performance was improved to a great extent. It was possible to record gratings with blue, green and red wavelengths in 130 μm thick films with more than 80% diffraction efficiency (DE) creating a refractive index modulation of $\sim 1.7 \times 10^{-3}$ at exposure energy of 50 mJ/cm^2. This material will be a good candidate for data storage and color holographic applications. One of the remarkable findings was that the storage and shelf life of the material could be extended compared to other photopolymer materials. This material could be used to write gratings with 70% DE even after 12 months of storage. Thus, addition of a second photosensitizer not only extended the absorption range, but also the shelf life of the photopolymer.

1. Introduction

Recently, photopolymers have grabbed much attention due to their application potential against other recording materials. Dry processing, ease of storing information, high diffraction efficiency, good spatial frequency response etc. make them fit for different holographic applications like data storage, information processing and display purposes. High refractive index modulation [1–3], good light sensitivity, real-time image development [3–5], high optical quality and low cost are the important properties of photopolymers enabling them to occupy an outstanding position as holographic recording media. One of the remarkable advantages of these photopolymers is the tunability of its spectral sensitivity or energy sensitivity by modifying the composition of different chemical constituents in the photopolymer solution [3,6].

The development of new photopolymer materials for a technologically developing world is an inevitable necessity. Photopolymer usually consists of a polymeric binder, monomer, photoinitiator system, crosslinker, and sensitizing dye [7,8]. The major difficulty in polymerization process is to design a highly efficient initiation system to improve the holographic properties of the material. The polymer binder acts as the supporting matrix encompassing the additive components. The monomer serves as the governing species to control the index modulation, induced by optical interference [7]. Initiation of polymerization starts when the dye absorbs incident light (here, interfering light) producing free radicals which in turn results in a spatially nonuniform monomer polymerization. The combination of nonuniform polymerization and free-monomer diffusion from destructive to constructive interference region creates a spatial modulation of the refractive index, which acts as the grating [9].

Along with other parameters, stability of the recorded information (storage life) and steadiness of the developed material (shelf life) are two important parameters in holography [10]. Many reports are available regarding the improvement of these parameters with modifications in the photopolymer compositions, like adding crosslinkers or metal ions like - Copper, Chromium, Silver, Nickel, Iron etc. by sacrificing or negotiating with energy sensitivity or other holographic properties [11–19].

Apart from the resistance to degradation on aging, response of an imaging media towards the entire visible region was always a

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question of interest from the emergence of such technologies. In photopolymers, extension of spectral response towards entire visible spectrum was usually done with a group of sensitizer additives such as dyes or metal ions with an inactive binder matrix [20–23,12,13]. The selection of sensitizers was done without compromising holographic performance of the material such as high spectral sensitivity, good diffraction efficiency, good spatial frequency response, storage life of the recorded data and shelf life of the material, etc. [10,24]. Quality of the developed films was ensured by optimizing the concentration of the sensitizers in the photopolymer solution. Incorporation of Silver and Nickel ions into Methylene blue (MB) sensitized poly (vinyl alcohol) films could improve the storage life and sensitivity of the developed films but longevityof the material was not much enhanced. The presence of metal ions could extend the absorption range of photopolymer samples and it was able to record gratings with blue, green and red wavelengths in these materials [12,13,23].

Tsuchida et al. [25] studied the stability of different sensitizing dyes and it was observed that among all the dyes studied, eosin (EY) was found to have better stability. Our study on eosin sensitized poly (vinyl alcohol)/acrylamide films also confirmed the same result by storing gratings for more than a year with good stability [10]. But shelf life of the samples got deteriorated after 5 months of storage. The main reasons may be the unwanted polymerization by stray light radiation, interaction with oxygen, inhibiting proper polymerization and also direct contact with environment [20,21,26,27]. Fimia et al. studied the effect of mixture of dyes (MB and Rose Bengal) in the photopolymerization kinetics of Poly (vinyl alcohol)/acrylamide system and they could span the absorption spectra towards the entire visible range. Thus, in addition to the elimination of inhibition by oxygen, they could establish panchromaticity in photopolymer samples [20]. In 2010, Meka et al. developed PVA based panchromatic photopolymer for multicolour reflection holography using three dyes (MB, Erythrosin B, Acriflavine) to absorb in the entire visible region [28]. Huang et al. reported the EY and MB dye combination and used 632.8, 514.5, 496.5 and 488 nm lasers for holographic characterization [29]. They could achieve only a maximum DE of 55% even with a layer thickness of 250 μm using 632.8 nm wavelength and all other wavelengths showed DE below this value.

The present work portraits the behavior of eosin doped Poly (vinyl alcohol)/ Acrylamide (EPVA) material when another dye, methylene blue (MB) was incorporated into this photopolymer system. By the inclusion of MB to the EPVA system, it was possible to extend the absorption range towards red region with a sustained holographic performance on aging. Holographic characterization was done using 632.8, 532 and 488 nm wavelength lasers and it was seen that incorporation of a second dye enhanced the overall holographic performance of EPVA system.

2. Materials and methods

For the preparation of photopolymer mixture, a 10% poly (vinyl alcohol) (Mw = 1, 25000), solution was used. To the PVA solution, 0.38 M acrylamide (AA-monomer), 2.8×10^{-2} M triethanolamine (TEA-Co-initiator/electron donor) was added. To this solution, eosin and methylene blue were added at a dose of 3×10^{-5} M and 1.4×10^{-5} M respectively, which were optimum values of these dyes described previously [10,24]. Concentrations of these dyes were varied and optimized according to the holographic performance of the developed samples. The mixture was stirred well to get a homogeneous solution. Polymer films were cast on glass plates kept on a leveled surface using gravity settling. The slides were kept protected from dust and dried at room temperature for more than 24–48 h. Thickness of the dried film was found to be 130 ± 2 μm measured using stylus profilometer (Dektak 6M). Absorption spectra of the prepared samples were recorded using JASCO V-570 UV-Visible-NIR spectrophotometer and compared with the mixture of dyes and with individual dye doped samples. Holographic gratings were recorded on the dried films using double beam interferometry with an incident intensity of 1.8 mW/cm^2 and in all cases DE measurements were conducted by passing a low power (1 μW) He-Ne laser beam (wavelength 632.8 nm) through the recorded gratings, kept at Bragg angle. The DE was calculated as,

$$DE(\%) = \frac{I_d}{I_i} \times 100$$

where,

I_d - Diffracted beam intensity,

I_i – Incident beam intensity

Storage life of the grating was determined by measuring the DE of the grating each day after recording of the grating while shelf life of the sample was examined by recording gratings in successive months from the date of sample preparation. The recorded films were kept inside a dark box and no post-exposure was applied. During the period of storage, the temperature of the storage place was in the range 28–30 °C and relative humidity was 45–65%.

3. Results and discussion

3.1. Absorption studies

Absorption studies showed that addition of methylene blue to the EPVA has extended the absorption window to red region. In the previous reported work using eosin doped PVA, a maximum DE of 85% was obtained using 488 nm laser [10] and in methylene blue doped PVA [24], a maximum DE of 75% was obtained using 632.8 nm. For the present study, initially the same dye concentrations reported in the above references were used. Samples were prepared using eosin and methylene blue mixed (EM) polymer solution and after drying absorption studies were conducted.

Fig. 1 shows the characteristic absorption of both the individual dyes and mixture of dyes. The major criterion in such mixing is to ensure the homogeneity of the mixed system.

The absorption spectra of EY and MB showed maxima at 528 nm and 660 nm respectively. It is interesting to note that when both these dyes were mixed, the material showed good

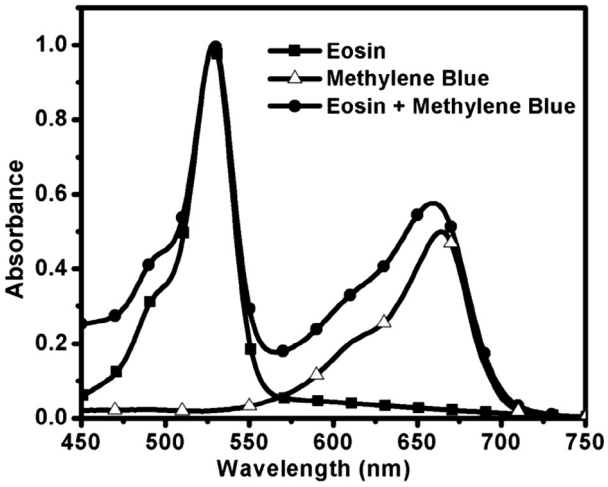

Fig. 1. Absorption spectra of EY, MB and EM samples.