CHAPTER 4

FORMATION OF HOLOGRAPHIC GRATING AND DIFFRACTION EFFICIENCY STUDIES ON THE DYE DOPED GELATIN THIN FILMS

4.1 INTRODUCTION

In this chapter, formation of grating and diffraction efficiency studies carried out in four different organic dye doped gelatin thin films as holographic recording medium are presented. A study on the dependence of the diffraction efficiency on various parameters has been studied and demonstrated.

NLO polymeric materials have been identified as strong candidates for emerging photonic data processing technologies. In general these materials consist of molecular fragments displaying NLO activity or highly colored chromophores, covalently attached to a polymeric host material. Organic dyes fixed on solid matrices are of interest for holographic recording. In the holographic process, the combination of guest dye with the host matrix plays an important role. The action of light induces and enhances photochemical changes in refractive index and/or absorption co-efficient of the host matrix and guest dye. Gelatin is an excellent medium for holographic storage. Dichromate sensitized gelatin was used with Ar-ion and He-Cd lasers (Ramenah et al 1996), while methyl blue sensitized gelatin was used with He-Ne lasers (Solano et al 1987) for holographic recording. The recording was in volume, and highly efficient holograms were recorded.
In the present study, four dyes (Fluorone dyes namely, acid red 92, acid red 94 and Azo dyes namely, acid red 29, acid red 1) embedded in gelatin have been used as holographic recording media.

### 4.2 EXPERIMENTAL SET-UP FOR THE FORMATION OF GRATING

The storage capacity of the films prepared can be verified by formation of grating. The ideal recording material for holography should have a spectral sensitivity well matched with available laser wavelengths. The optical set-up used for recording the grating is shown in Figure 4.1.

![Figure 4.1 Experimental setup for grating recording](image)

**Figure 4.1 Experimental setup for grating recording**

(BS - Beam splitter, M1, M2, M3 and M4 - Mirrors, PD - Photo detector)

The 532 nm wavelength of cw Nd-YAG laser (Compas™215M, COHERENT) has been used as the light source to record gratings. The beam diameter of the laser is 0.32 mm. The output wavelength (532 nm) is very close to the peak of the absorption band of the dyes under study (UV-Vis absorption spectra of the dyes under study are presented in Table 2.1).

The beam from the laser is divided into two beams using a dielectric coated beam splitter. These two beams are allowed to superpose and
the dye doped gelatin film is placed at the region of superposition. A permanent grating formation is observed. The experiment is performed on a vibration isolation table. The spatial frequency of the grating is easily changed by changing the angle of interference.

The growth of grating is monitored by illuminating the region of superposition with a He-Ne laser (Research Electro Optics-30995) beam in transmission mode and the intensity of the first order diffracted beam is monitored with a photo detector (LM2, Coherent Inc.) connected to a power meter (FieldmasterTM GS, Coherent Inc.).

4.3 RESULTS

4.3.1 Diffraction Efficiency Studies on Fluorone and Azo Dye Doped Gelatin Thin Films

Highly efficient materials are preferred for a good recording. The diffraction efficiency of the grating is the ratio of the intensity of the first order-diffracted power to the incident read beam power. The grating formation is found to depend on

1. Time of exposure.
2. Concentration of the dye doped gelatin film.
3. Intensity of the interfering beams.
4. Intensity ratio of the interfering beams.
5. Spatial frequency.

4.3.1.1 Grating formation as a function of dye concentration in thin gelatin films

The recording plate is placed at the point of intersection of two writing beams split from cw Nd:YAG laser (532 nm), with gelatin side facing
The beams. Unexpanded beam from a He-Ne laser is incident normally at the region of superposition.

Grating formation dependence on the dye concentration is studied with different dye concentration plates. Dye doped gelatin plates with different doping concentrations are prepared by soaking the gelatin plates in 20, 25, 30, 35 mM of the dye solutions for 5 minutes. The plates with different concentrations are expressed in terms of optical density (OD) instead of concentration. The transmittance of films corresponding to different concentrations are given in Table 4.1.

Table 4.1  Optical density of the dye-doped gelatin films with different dye concentrations at 490 nm

<table>
<thead>
<tr>
<th>Dye concentrations (mM)</th>
<th>Optical density (OD) of the dye-doped gelatin films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid red 94</td>
</tr>
<tr>
<td>20</td>
<td>0.405</td>
</tr>
<tr>
<td>25</td>
<td>0.487</td>
</tr>
<tr>
<td>30</td>
<td>0.565</td>
</tr>
<tr>
<td>35</td>
<td>0.700</td>
</tr>
</tbody>
</table>

These plates are exposed to interference pattern and the intensity of first order-diffracted beam is measured continuously for 30 minutes, maintaining the power of the writing beams at 18 mW and the angle between the interfering beams at 20°. The variations of the intensity of the first order-diffracted beam for different concentrations of the four samples are graphically presented in Figures 4.2 to 4.5. It is observed that the rate of formation of grating increases with increase in the concentration for the dye doped gelatin film. The diffraction efficiency of the grating reaches a maximum value and then starts decreasing. This may be due to the degradation of the grating structure after reaching the saturation value due to
over exposure. The diffraction efficiency values of the corresponding curves are tabulated in Table 4.2.

Figure 4.2  Variation of the first order diffracted power Vs time of acid red 92 dye at different concentrations

Figure 4.3  Variation of the first order diffracted power Vs time of acid red 94 dye at different concentrations
Figure 4.4  Variation of the first order diffracted power Vs time of acid red 29 dye at different concentrations

Figure 4.5  Variation of the first order diffracted power Vs time of acid red 1 dye at different concentrations
Table 4.2  Diffraction efficiencies of dyes doped gelatin film for different concentrations

<table>
<thead>
<tr>
<th>Dye Doped gelatin film</th>
<th>Diffraction Efficiency ( % ) at 50:50 and θ=20°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 mM</td>
</tr>
<tr>
<td>Acid red 92</td>
<td>0.520</td>
</tr>
<tr>
<td>Acid red 94</td>
<td>0.730</td>
</tr>
<tr>
<td>Acid red 29</td>
<td>0.355</td>
</tr>
<tr>
<td>Acid red 1</td>
<td>1.078</td>
</tr>
</tbody>
</table>

4.3.1.2 Grating formation as a function of spatial frequency

Resolution and storage capability of materials are important factors determined by the spatial frequency. The first order diffraction efficiency has been investigated as a function of spatial frequency and the results are shown in Figures 4.6 to 4.9 for samples acid red 92, acid red 94, acid red 29 and acid red 1, respectively. The angle between the interfering beams is varied to be 10°, 20°, 30° and 40° and the effect of the change in the efficiency of the grating formation is studied. The fringe spacing (Λ) is calculated by equation (4.1).

\[ \Lambda = \frac{\lambda}{2\sin(\theta/2)} \] (4.1)

where \( \lambda \) and \( \theta \) are the wavelength and incident angle of the writing beams, respectively. By changing \( \theta \) from 10 degrees to 40 degrees, \( \Lambda \) is varied from 3.05 \( \mu m \) to 0.77 \( \mu m \) and the corresponding spatial frequency changes from 328 to 1282 lines mm\(^{-1}\). The maximum diffraction efficiency was observed at an angle of 20 degrees.
Figure 4.6 Variation of first order diffracted beam power Vs time for different angles between the writing beams for acid red 92 dye doped gelatin film.

Figure 4.7 Variation of first order diffracted beam power Vs time for different angles between the writing beams for acid red 94 dye doped gelatin film.
Figure 4.8  Variation of first order diffracted beam power Vs time for different angles between the writing beams for acid red 29 dye doped gelatin film

Figure 4.9  Variation of first order diffracted beam power Vs time for different angles between the writing beams for acid red 1 dye doped gelatin film
Figure 4.10 illustrates the relationship between the power of the first order-diffracted beam and the angle between the writing beams for all the dyes under study. The diffraction efficiency values corresponding to the curves are presented in Table 4.3.

![Figure 4.10 Power of the first order-diffracted beam as a function of the angle between the writing beams for the dyes under study](image)

<table>
<thead>
<tr>
<th>Dye Doped gelatin film</th>
<th>Diffraction Efficiency (%) at 35 mM concentration and 50:50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10°</td>
</tr>
<tr>
<td>Acid red 92</td>
<td>0.470</td>
</tr>
<tr>
<td>Acid red 94</td>
<td>0.750</td>
</tr>
<tr>
<td>Acid red 29</td>
<td>0.240</td>
</tr>
<tr>
<td>Acid red 1</td>
<td>0.960</td>
</tr>
</tbody>
</table>
4.3.1.3 Grating formation as a function of intensity ratio of the writing beams

Ascertaining that the intensities of the writing beams remained practically constant for the entire recording period, experiments have been conducted by varying the intensity ratio of the writing beams. The fringe contrast depends on the intensity ratio and hence this parameter becomes important. The rate of formation of the grating is monitored by measuring the diffracted intensity in the first order. Figures 4.11 to 4.14 show the variation of the first order diffracted intensity with time for three different intensity ratios (50:50, 60:40 and 70:30) for samples acid red 92, acid red 94, acid red 29 and acid red 1, respectively. As expected the diffraction efficiency is found to be maximum for an intensity ratio of unity (50:50). The diffraction efficiency values of the corresponding curves are given in Table 4.4.

Table 4.4 Diffraction efficiencies of dyes doped gelatin film for different intensity ratio of the interfering beams

<table>
<thead>
<tr>
<th>Dye Doped gelatin film</th>
<th>Diffraction Efficiency ( % ) at 35 mM concentration and θ = 20°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50:50</td>
</tr>
<tr>
<td>Acid red 92</td>
<td>0.623</td>
</tr>
<tr>
<td>Acid red 94</td>
<td>1.030</td>
</tr>
<tr>
<td>Acid red 29</td>
<td>0.378</td>
</tr>
<tr>
<td>Acid red 1</td>
<td>1.319</td>
</tr>
</tbody>
</table>
Figure 4.11 Power of the first order-diffracted beam as a function of intensity ratio for acid red 92 dye doped gelatin film.

Figure 4.12 Power of the first order-diffracted beam as a function of intensity ratio for acid red 94 dye doped gelatin film.
Figure 4.13 Power of the first order-diffracted beam as a function of intensity ratio for acid red 29 dye doped gelatin film

Figure 4.14 Power of the first order-diffracted beam as a function of intensity ratio for acid red 1 dye doped gelatin film
4.4 COMPARISON

Figure 4.15 shows the relationship between the power of the first order-diffracted beam Vs time for different dye doped gelatin films under study. All the films have been prepared by doping the gelatin in 35 mM concentration of the dye for 10 minutes. The intensity of each writing beam is kept constant at 18 mW and the angle of interference is 20°. The results of all the four dye doped plates are compared in Figure 4.15. It is observed that, acid red 1 sample is more efficient followed by acid red 94. Diffraction efficiencies of 1.319 %, 1.020 %, 0.620%, and 0.385% have been observed in acid red 1, acid red 94, acid red 92 and acid red 29 films, respectively.

![Graph showing comparison between four dyes doped gelatin films](image)

**Figure 4.15  Comparison between the four dyes doped gelatin films**

4.4.1 Model for Grating Formation Mechanism

Surface relief grating recording has been reported in side chain dye polymers. Rochon et al (1995) have attributed the formation of grating due to thermally driven mass diffusion mechanism in poly(4’–{[2–(acryloyloxy)thel]ethyl–amino}–4–nitroazobenzene) polymer thin film.
Photo-induced viscoelastic flow in amorphous high-TG polymers based on a substituted azobenzene side group was observed by Barret et al (1996). Jiang et al (1996) have proposed that the macroscopic motion of polymer chains is due to the interaction of dipoles with internally generated fields, as chromophores are continuously cycled through the trans-cis-trans isomerisation.

In the present study, where the materials used for recording are acid red dye doped gelatin films, the following model is proposed. When the films are exposed to interference pattern, in the bright region the dye molecule absorb the light energy and get excited to singlet, which decays rapidly to the triplet states. Since the energy is high enough, the molecules in the triplet state are further excited and dissociated into free radicals of high volatility (Finer 1994). Due to this type of "homolytic fission of carbon-carbon single bonds", the concentration of dye molecules in the bright region decreases reducing the thickness of the film. Surface relief formation can thus be attributed to dissociation of dye molecules. This results in inscribing of permanent surface relief grating structure. It is also observed that the rate of formation is more when free surface is exposed to the interference pattern. Instead if the interfering beams reach gelatin through glass-gelatin interface for grating formation, more power of the writing beams is required and moreover the diffraction efficiency is found to be considerably less. The free surface requirement confirms the formation of surface relief grating in addition to the modulation of absorption due to dissociation of dye molecules.

When a grating written area is exposed to uniform and intense laser radiation at the same wavelength used for writing ($\lambda = 532$ nm), the grating structure disappears. This can be attributed to the total bleaching of the dye molecules in the exposed area. Hence erasure and rewriting is not possible in the written area in these materials.
4.5 ATOMIC FORCE MICROSCOPIC OBSERVATION

Atomic Force Microscopic investigations of a grating structure recorded in acid red 1 film are carried out. AFM scans are made with Nanoscope III (CA, USA) on the recorded spot. AFM picture recorded on the exposed interference pattern reveals the creation of surface relief, as shown in Figure 4.16. The three dimensional view of the surface gratings as obtained by AFM measurement shows sinusoidal surface relief structures with a period of 5.7 µm which is consistent with the optical microscopic observation. The depth of the surface relief pattern is about 55 nm. This therefore confirms that recording is in the form of thickness modulation.

Figure 4.16 Three-dimensional view of AFM picture of the surface relief grating structure on the acid red 1 dye film showing sinusoidal variation of depth

The process of grating recording (ablation) would reduce the thickness of the film in the region of high intensity. In this grating, a
sinusoidal light intensity spatial variation produces a sinusoidal profile. The surface modulation profile formed is linearly related to the light intensity distribution at the surface of the film. Figure 4.17 shows the two dimensional view of AFM picture recorded after the grating formation.

Figure 4.17  Atomic Force Microscope scan on the surface of acid red 1 dye soaked gelatin film after grating formation

4.6 CONCLUSION

Acid red 1 and acid red 94 dye soaked gelatin films are found to be good media for holographic recording. It is observed that the formation of grating strongly depends on the intensity ratios of the writing beams, the concentration of dye in the film and the angle between the writing beams. Diffraction efficiency of 1.319 %, 1.020 %, 0.620%, and 0.385 % have been observed in acid red 1, acid red 94, acid red 92 and acid red 29 films respectively. Efficient writing can be made at an angle of 20° keeping the intensity ratio of the writing beams unity (50:50).
Comparison of results indicates that acid red 1 dye soaked gelatin films have higher diffraction efficiency than the other three dye soaked films under identical recording parameters. Up to three diffraction orders have been observed. A model has been proposed to explain the mechanism of the formation of surface relief grating. The diffraction efficiency of the grating is found to remain unchanged even after a storage period of several years.