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Study of the behavior of holographic gratings as a function of voltage

by

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Abstract

The continuous research and development of photosensitive materials such as holographic recording medium, plays an important role in holography. For several years, the research group of Holography and Materials Laboratory of this institution has been studying conducting polymers as photosensitive materials for holographic recording. The results have generated new lines of research as described in this paper, by studying the behavior of holographic gratings in dichromated polyvinyl alcohol doped with nickel chloride by applying a voltage.

Whereas the ability to record real-time holographic with this material and response modulation by applying a voltage during the formation of holographic gratings, the changes in the diffraction efficiency is the most important information of the study. The development of photosensitive plates hydrophilic matrix polymer polyvinyl alcohol and sensitizing agents are used to holographic recording, and the study of the diffraction efficiencies of real-time as a function of voltage, allows us generate new knowledge related to the development of photosensitive materials such as holographic recording media and contribute to the strengthening of the research area of holography and materials on this institution.

The experimental results, discussion and conclusions are explained by the diffraction efficiency as a function of voltage, thickness, spatial frequency and relative humidity.

Resumen

La continua investigación y desarrollo de materiales fotosensibles como medio de registro holográfico, juega un papel importante en holografía. Desde hace varios años, el grupo de investigación del Laboratorio de Holografía y Materiales de esta institución ha estado estudiando polímeros conductores como materiales fotosensibles para el registro holográfico. Los resultados obtenidos han permitido generar nuevas líneas de investigación como la que se describe en este trabajo, a partir del estudio del comportamiento de rejillas holográficas en alcohol polivinílico dicromatado dopado con cloruro de níquel con la aplicación de un voltaje.

Considerando la capacidad de registro holográfico en tiempo real de este material y su respuesta de modulación con la aplicación de un voltaje durante la formación de las rejillas holográficas, destacamos los cambios en la eficiencia de difracción. El desarrollo de placas fotosensibles de una matriz hidrófila de alcohol polivinílico como polímero soporte utilizando agentes sensibilizantes para el registro holográfico; y el estudio de las eficiencias de difracción en tiempo real como función del voltaje, nos permite generar nuevos conocimientos relacionados con el desarrollo de materiales fotosensibles como medios de registro holográfico y contribuir en el fortalecimiento del área de investigación de holografía y materiales de esta institución.

Los resultados experimentales, discusión y conclusiones están en función del estudio de las eficiencias de difracción como función del voltaje, espesor, frecuencia espacial y humedad relativa.

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Mi hija, mi esposo y
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Chapter 1

Introduction

The significant progress of materials development and their applications plays a major role in holography as holographic recording media. The continuous investigations are always looking to get better materials with fewer resources and less cost which result in the development of such materials.

The investigation of holographic materials to record at real time has been considered for holography research teams in the world. For several years, a group of materials and holography laboratory researchers of Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE) has been studying the photopolymers as holographic recording material.

This thesis comes from the need to develop a new photopolymer material to holographic gratings where the application of voltage plays a significant role in the response modulation of real time diffraction efficiencies. The characterization of this photosensitive material shows significant results which in turn needs to be optimized, but currently our photopolymer can be used as holographic recording material.

The main objective of this investigation is study the behavior of holographic grating as a function of voltage in a new photopolymer material which is composed of a polymer matrix (polyvinyl alcohol), dichromate and nickel chloride. To achieve this goal it is

necessary to cover particular objectives that determine the content and structure of the results:

- Identify the composition of the photosensitive material.
- Calculate the thickness of film.
- Quantify the diffraction efficiency.
- Study the influence of voltage.
- Study the influence of relative humidity.
- Establish the Module of Transfer Function (MTF).
- Calculate the photosensitivity of the material.

The innovation of this research is the response modulation due to application of a voltage during the formation of holographic gratings in dichromated polyvinyl alcohol doped nickel (II) chloride hexahydrate, which complement the knowledge in holographic recording materials.

This work is divided on five chapters, which contain the basic information to locate in the context of our investigation. The objectives will be achieved through the definition of experimental process and discussion of results. The chapters are structured as follows:

Chapter 1 is the current section that deals about introduction of research project where the motivation and objectives are specified.

Chapter 2 deals to most important holographic parameters to photosensitive recording media and the most common media to record holograms.

Chapter 3 explains the general characteristics of photopolymer systems used as recording media and the photopolymerization process to holographic recording. The self-enhancement and crosslinking processes are also referred as very important role to diffraction gratings formation.

Chapter 4 refers to preparation of the photopolymer material which is used as recording media. The synthesis of new materials is not simple and the way that it carried out to produce the films plays an important role in the formation of the holographic gratings. The composition of photosensitive media and thickness film is two major parameter used for this investigation in the study of diffraction efficiency and holographic formation.

Chapter 5 describes the optical setup used for experimental testing of holographic recording, the experimental results and discussion. The results of holographic gratings are studied for diverse parameters as spatial frequency, thickness film and composition of coating solution, with and without voltage application. The intensity of recording beam take part in a significant role to holographic formation due to the fact that it produces a considerable enhance in the rate of photopolymerization and consequently good diffraction efficiency results.

Chapter 6 discusses about the results and Chapter 7 describes the conclusions obtained from this research and the futures investigations.

Chapter 2

Holographic recording medium

The development of new recording media is very important to the advance of holography. This section describes the main holographic parameters to photosensitive material which can be used as recording media and we will use to present the results at real time. There are a lot of photosensitive materials used in holography. In this chapter we will explain briefly the most common material used as recording media.

2.1 Requirements of holographic recording media

The main parameters of recording media to determine the possibility of their use in holography are [2.1]:

(1) The efficiency of information reading is determined by the brightness or the diffraction efficiency (η) of holograms [2.2]. The diffraction efficiency is the ratio of the diffracted intensity and the incident intensity of the probe beam and is associated with refractive index modulation n [2.3]

$$\eta = I_{dif} / I_{inc} = I_{+1} / I_0 , \quad (2.1)$$

where $I_{dif} = I_{+1}$ is the intensity of the light wave of the first diffraction order and $I_{inc} = I_0$ is the incident light intensity.

The highest value of diffraction efficiency is achieved only for phase holograms that do not absorb restoring light; this is possible only in the case of recording media change their refractive index or thickness under the action of light [2.1].

(2) Sensitivity (S) of the medium can be defined as the ratio of square root of diffraction efficiency and exposure energy (E) per unit area [2.4].

$$S_1 = \frac{\eta^{1/2}}{E} [cm^2 / J] \quad (2.2)$$

Sometimes, it can be useful to calculate the sensitivity per unit of material thickness (d) [2.4].

$$S_2 = \frac{\eta^{1/2}}{Ed} = \frac{S_1}{d} [cm / J] \quad (2.3)$$

(3) Angular sensitivity [2.1]

$$\theta = \Lambda/d, \quad (2.5)$$

where $\Lambda = 2\pi K$ is the period of the holographic diffraction grating and d is the thickness of the photosensitive medium.

The maximum angular sensitivity determines the capability of writing and reading holograms in the same area of the layer is achieved only for layers of large thickness [2.3].

2.2 Types of recording medium

Holographic recording material has been attracting strong interest to research and applications on digital recordings and watermarking [2.5-2.7]. The optimization of all types of recording materials is connected to their application [2.8].

There are a lot of photosensitive materials used in holography where each one of them has a different way to absorb light. The most familiar materials used to holographic recording are the following:

- **Dichromated gelatin (DCG)** consists of a layer of gelatin with Cr^{+3} ions which are sensitive to light. Ions that absorb light will modify the gelatin in their neighborhood, so finally the refractive index modulation is obtained in this gelatin. Special attention is placed to the sealing of these emulsions after processing to ensure they stay unchanged form [2.9]. The oldest holographic material is the best photosensitive recording material used in holography, leading to high quality holograms and high signal/noise ratios [2.10]. DCG is used for manufacturing holographic optical elements with high diffraction efficiencies because it has an excellent signal to noise ratio and high environmental stability [2.8].
- **Thermoplastics** use a plastic material which surface can be loaded with a uniform distribution of charge. The recombination of the charges is directly proportional to the amount of light incident on the material. This material is revealed by heating; the plate deforms in proportion to the accumulated charge [2.9]. They are excellent

real time materials for holographic interferometer, reusable and quality images production [2.8].

- **Photoresist** is a material that records the information light by modulation of relief. It has the ability to be soluble (positive) or insoluble (negative) in an organic solvent, after being exposed to short wavelength light radiation [2.9].
- **Silver halide emulsion** is constituted by a support which is a glass plate or a plastic sheet over it there is a layer of gelatin a few micrometers thick, which is a suspension of silver halide particles, also incorporated sensitizers the emulsion. Once exposed the emulsion is subjected to a developing process. [2.9]
- **Photorefractive** is a holographic recording media can be used a theoretically infinite number of times and it requires no additional processing (developing, fixing, etc.). Light induces a redistribution of charges within the crystal, so in a characteristic time, establishing a dynamic equilibrium between the internal distribution of electrical charges. The variation in the distribution of these charges in turn causes a variation in the refractive index of the material matrix by electro-optical effect, leading to the formation of a volume hologram with phase modulation. [2.9]
- **Photopolymers** consist of a mixture of monomers where the polymerization reaction is catalyzed by light. In addition the monomers, it is included sensitizers,

which contribute to the initiation of polymerization reactions. [2.9] The main advantages of using dry photopolymers are self-developing capability, shape flexibility, low cost, large-area processability [2.11-2.12], high angular selectivity and high resolution that make them more suitable for applications [2.13-2.14].

Table 2.1 shows some important optical characteristics of different materials that have been studied in holographic [2.15].

Table 2.1 Summarize of some materials as holographic media and principle parameters. [15-16]

Material	Volume / Surface	Sensitivity		Storage Density (Lines/mm)	Response time	Thickness (mm)	Stability	
		Spectral range (nm)	S (cm/J)				Rewrite	Temperature range (°C)
Organic								
Cationic ring Photopolymerization	V	514, 532, 650-670	0.5-6.7x10 ³			100-500	No	
CL and amorphous polymers with azobenzene / photoisomerization	V/S	488, 514, 532, 633		> 6000		2-10	Si	< 100
CL and amorphous polymers with azobenzene / surface reliefs	V/S	257-532	10 ²	> 3000	1000s	3-5	Si	
Photochromic	V/S	Visible	3x10 ²	> 1600	ms	100		
Dye-doped nematic LC / reorientation of surface	S	440-514	3 x 10 ³	> 1000	ms	10-20	No	
PDLC/PIPS/TIPS/ Photorefractive	V/S	360-532 770-870		> 1000		20-100	No PIPS/TIPS/PR	
PALC / Photochemical phase transition	V/S	< 550	10 ⁴	> 1000	100ms	0.2-1.2	Si	< 48-95
Bacterio-rhodopsin in gelatin matrix	V/S	520-640	4.7x10 ⁶	> 1000	1-100ms	30-40	> 10 ⁶	-20 / 40
Dichromated gelatin	V	< 700	10 ⁴	> 5000		15-35	No	
Other photopolymers	V/S	< 550	10 ³	> 5000	10s-2min	5-500	No	
Films of sol-gel	V	< 550	6.3x10 ²	> 2000	s	100-1500	No	
Acrylamide-based photopolymer	V	510-540 590-690	8x10 ³	> 3000	0.1-0.2 s	65-150	No	
Inorganic								
Silver halide	V/S	< 800	1100	> 7000		(7-8)	No	
LiNbO ₃	V	350-650 800-1000	0.02-0.1 0.02-40	> 2000	0.5-20 s	> 10 ³ 000	Si	
LiTaO ₃	V	300-550		> 2000	0.1- 20 s	> 10 ³ 000	Si	
KnbO ₃	V	400 – 900	30-3000	> 2000	1 ms – 1 s	> 10 ³ 000	Si	
Sn ₂ P ₂ S ₆	V	550-1100	1000-5000	> 2000	0.5 – 500 ms	> 10 ³ 000	Si	
Bi ₂ TeO ₃	V	450-550	0.5	> 2000	ms			< 100

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Chapter 3

Recording media: Photopolymer

Photopolymers have shown optimal properties to record information in real time without chemical process to get a picture. These materials have been obtained more recording capacity, light sensitivity, durability, resolution and longer life for the stored information.

The development of photopolymer materials has become one of the most dynamical developing branches of holography [3.1-3.5]. Holographic recording in organic polymer materials has been studied intensively in the hope that these materials could yield efficient, low cost and high storage materials [3.6].

In this section, the fundamental theory of holographic recording with photopolymer is explained. The photopolymer systems and the photopolymerization process used as recording media to hologram formation are described. Also, the self-enhancement and crosslinking process are discussed.

3.1 Photopolymerizable materials

Photopolymerizable materials (PPMs) usually include a multifunctional monomer or oligomer, a photoinitiating system (photoinitiator or photosensitizer), a polymeric binder,

and various additives that increase the photosensitivity of the recording medium (co-initiators). Figure 3.1 shows how polymer is formed in irradiated areas [3.7].

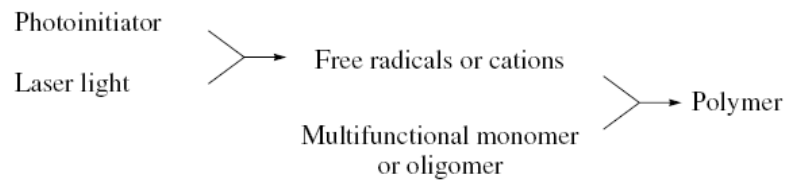


Figure 3.1 Polymer formations [3.7].

The process of light-induced radical polymerization is used in mechanisms of holographic formation in photopolymer recording materials [3.8-3.9]. The formation of a hologram in photopolymer mainly involves two factors polymer formation on areas exposed to light and the diffusion of monomer from the unexposed areas to neighboring areas exposed where part of the monomer has polymerized [3.10]. To obtain holograms, two photoinduced processes are used: (a) photoinduced change in the density of a photopolymerizable system [3.11] and (b) photoinduced diffusion of the components during irradiation [3.7].

The photoinitiating systems are one of the most important PPM components which include only a photoinitiator if holograms are written with short-wavelength laser light, or a mixture of an initiator and a photosensitizer in the case of recording holograms with long wavelength ultraviolet (UV) or visible light. [3.11]

The selection of monomers is based on the requirement that photoinduced changes in the refractive index, which depend on the difference between the refractive indexes of

the polymer matrix and the monomer [3.12]. During exposure period, the monomer diffuses into bright regions as a result of the concentration gradient induced by the depletion of these components [3.8]. This causes a further difference in density (and so refractive index) between bright and dark regions [3.13]. The exposed area could swell due the material mass transport [3.14].

A number of organic compounds are known as photoinitiators of radical and cationic photopolymerization [3.15]. The use of photoinduced forms of photochromic compounds as photosensitizers seems to be attractive [3.16-3.19]. The kinetic photopolymerization depends on the intensity of laser light [3.20] and efficiency depends on the nature of photoinitiators [3.7].

3.2 Photopolymerization process

The photopolymerization process of photopolymer system can be briefly explained as follows:

The photopolymer is irradiated by light and the photon energy is transferred to the photoinitiator to produce primary free radicals, which force to monomer molecules to form secondary free radicals. These secondary free radicals continuously react with monomers to grow a large polymer chain, so the refractive index in the exposure region (bright region) increases. [3.21]

The depletion of monomer molecules in the exposure region causes the monomer concentration gradients between the bright region and dark region. The diffusion of monomers from dark region to the bright region takes part in the photopolymerization reaction which will result in the increase in the refractive index in the exposure region and therefore the diffraction efficiency of holographic gratings. And finally when all the reaction processes are stabilized, the phase grating with refractive index modulation is formed. [3.21]

The physical mechanism of photosensitivity and spatial resolution enhancement by changing the environmental temperature and molecular weight of binder is discussed preliminarily as follows [3.21]:

(1) Polyvinyl alcohol (PVA) with low molecular weight can decrease the viscosity of photosensitive film; this will make the diffusion of monomers from dark region to bright region much easier and faster. The increase in diffusion speed will improve the photosensitivity.

(2) The increase of environmental temperature will also increase the rate of monomers' diffusion in photosensitive film so higher temperature means that more monomers are transferred from dark region to bright region during a certain period of time. As a result, the photosensitivity will be improved. But much higher environmental temperature will result in the decrease of diffraction efficiency.

3.3 Holographic recording

The photopolymers are one of the most promising holographic recording materials for its easy preparation, ability to achieve high diffraction efficiencies, low noise and relatively low cost [3.22].

The formation of holograms in this media is a nonlinear process depending on the ratio between the rates of diffusion of components and polymerization [3.23]. Further irradiation of the PPM layer with an incoherent or restoring reference laser beam leads to photopolymerization of the whole layer. As a result, non-uniform concentration of the polymer is formed in the layer, which provides writing holograms of two types: relief holograms and volume holograms or both effects on the same polymer matrix [3.24].

The PPM thickness determines the hologram recording conditions [3.25]. The thickness of the layers of material prepared for exposure determines the monomer concentration necessary to obtain high diffraction efficiency and whether the modulation occurs or not. Since the diffraction efficiency obtained is affected by the thickness of the material and the index modulation, for a given thickness, it is necessary to adjust the monomer concentration to delimit the refractive index modulation [3.26].

Upon exposure of laser light with holographic data photopolymerization can be initiated by absorbing energy, sensitizing dye and decomposition of initiators. Holographic exposure produces spatial diffraction patterns due to photoinitiated polymerization. [3.27]

The formation of the hologram takes place when the photoinitiator is excited by the illumination pattern, resulting in the formation of radicals. These highly reactive compounds produce a spatially non-uniform polymerization and as result of the concentration gradients produced, monomers diffuse from the dark regions to the neighboring bright regions. Thus, the spatial modulation of the refractive index and its evolution over time is the result of non-uniform polymerization and the diffusion monomers. [3.28]

The temporal variation of diffraction efficiency depends on the temporal conversion grade of monomer into polymer, so depending on the termination process. The response of the diffraction efficiency will be different in function to some physicochemical parameters, such as concentration of photoinitiator, monomer or intensity. [3.28]

In general, reflection patterns in light-induced polymerizing photopolymers are explained as in figure 3.2. At first, light beams with reflection pattern by positive and negative interferences illuminate the photopolymer film, and then photopolymerization takes place on the area of positive interference of light. Monomer diffusion takes place due to the concentration differences between photopolymerized zones of low monomer concentration and unpolymerized zones of high concentration [3.29].

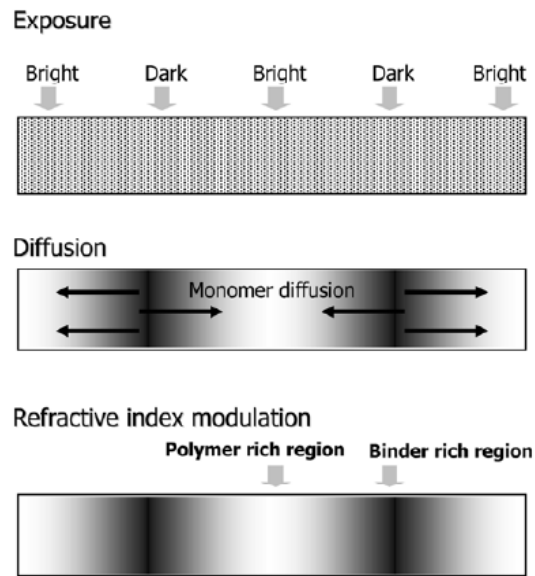


Figure 3.2 diffraction grating formations in holographic media after exposure. [3.29]

Polyvinyl alcohol (PVA) is used as binding polymer for photopolymers which is water soluble and so the film manufacturing is more convenient [3.30-3.35].

3.4 Self-enhancement

The self-enhancement of a hologram is the increase in its diffraction efficiency after the recording over time under light illumination or in the dark. Self-enhancement, during and after the recording can be considered as a two stage holographic recording method, which light illumination is profitable when the recording energy or the exposure time is limited [3.36], that corresponds an optimal exposition of energy. With dark reaction, the physicochemical processes are acting after exposure to achieve a balance.

The self-enhancement process can be characterized by the self-enhancement coefficient, $\xi = \eta_t/\eta_0$ and by the self-enhancement rate, $\beta = d\xi/dt$. Where η_0 is the initial diffraction efficiency immediately after the recording and η_t is the diffraction efficiency after time t [3.36].

The self-enhancement process [3.36] is explained when the Cr^{+6} are consumed slowly during photochemical reaction induced during the exposure. All the Cr^{+5} (produced by the reduction of Cr^{+6}) are not reduced to Cr^{+3} during exposure and this reduction continue in the dark; this reduction is large in the most exposed regions than in the least exposed region. Cr^{+3} or un-reacted Cr^{+5} may diffuse from the less exposed regions to the more exposed regions. Diffusion of Cr^{+3} ions is possible only if all the Cr^{+3} ions are not bound in the cross-linkage that form the matrix polymer.

The number of crosslinkage between Cr^{+3} and PVA increases and thus the index modulation also increases which induces a raise in diffraction efficiency. This dark reaction physicochemical process may be the major reason for the self-enhancement. [3.36]

The polymerization is not finished during the recording period. Polymerization continues bringing new cross-linkages with Cr^{+3} ions, which is responsible for the grating formation. The internal stress in the matrix polymer coating body increases during drying and exposure times. But when the coating expands by absorbing moisture at room temperature, the internal strain is relaxed and this also contributes to the increase in diffraction efficiency [3.36].

Polymerization and crosslinking contribute to the refractive index modulation, which leads to the grating formation [3.36]. The self-enhancement observed in dichromated polyvinyl alcohol (DCPVA) may be due to the dark reaction, diffusion, polymerization and internal stresses [3.37].

3.5 Crosslinking

The irradiation of dichromated systems causes two-step reduction of Cr^{+6} into Cr^{+5} and then into Cr^{+3} . The oxidation and the crosslinking of the host polymer occur in parallel. It is established that equilibrium with Cr^{+5} is an important radical, to obtain high quality of the hologram [3.38].

The reduction process was shown to be strongly influenced by the nature of the polymeric matrix. Cr^{+6} reductions took place in two successive and well-separated steps in DCPVA, $\text{Cr}^{+6} \rightarrow \text{Cr}^{+5} \rightarrow \text{Cr}^{+3}$, with only the involvement of photo-redox processes Cr^{+5} formed under irradiation are stable in DCPVA. [3.39].

The formation of the carboxylate groups, which is stoichiometrically parallels the reaction producing Cr^{+3} , depends on the nature of the polymeric matrix. In DCPVA, the carboxylate groups are secondary photoproducts. They are obtained from the oxidation of the polymer corresponding to the slow step of the reduction, $\text{Cr}^{+5} \rightarrow \text{Cr}^{+3}$ [3.39].

In DCPVA, the reticulation involves a complex reaction of Cr^{+5} , which acts as a bridge between the macromolecular chains, and of Cr^{+3} at longer exposure times [3.40]. The formation of Cr^{+3} was accompanied by the formation of carboxylate groups [3.41]. The branching and crosslinking of polymers improves the stability of the recorded hologram [3.42].

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Chapter 4

Preparation of photopolymer films

The development of new materials to holographic recording demand continuous experimental tests, great infrastructure and lots of resources to achieve the objectives set. The preparation of new materials is not simple, because most of the time, the limited resources affect the performance and the delivery times have been gradually displaced.

There are other variables that can affect the rate of research and full compliance with the objectives as the differences between the results observed and expected according to available information. The feedback process allows achieving reliable and reproducible results, increasing the response time to the issues raised and successful completion the project.

Based on the above, in this section we will give details about the experimental process to make our photopolymer to holographic recording. It includes the components of materials and the preparation of recording media according to requirements to achieve the objectives and expectation of results.

4.1 Photosensitive films

A new generation of photopolymer system is studied in this research, which has a different composition respect to literature, in order to make possible the

photopolymerization maintaining the properties of the holographic recording material such as its response to changes in spatial frequency and diffraction efficiency.

Photopolymer components of our photosensitive film are polyvinyl alcohol (PVA), potassium dichromate (PDC), nickel (II) chloride hexahydrate (Ni^{+2}) and glycerol (Gly). The characteristics of each component are showed in table 4.1. The photopolymer obtained is dichromated polyvinyl alcohol doped with nickel ions (DCPVANi) which does not require chemical or thermal processing.

Table 4.1 Characteristics of photopolymer components. [4.1]

Components	Chemical Formula	Trademark	Purity (%)	Molecular Weight (g/ml)	Solution Composition (% wt/wt)
PVA	$(\text{C}_2\text{H}_4\text{O})_x$	Meyer®	95.0	30000	7
PDC	$\text{K}_2\text{Cr}_2\text{O}_7$	Baker®	99.0	294.19	10
Ni^{+2}	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Baker®	97.0	237.71	10
Gly	$\text{C}_3\text{H}_5(\text{OH})_3$	Meyer®	99.8	92.10	100

The selection of the components is based for the availability of these supplies in the Laboratory and the safe handling. Moreover, in the last few years a number of groups has been studied the formation of conductive organic material based on PVA and sensitizer elements as metallic chlorides, ammonium dichromate and complexing constituent as glycerol; in order to taking advantage of the electrical and electronic characteristics that this type of materials can be provide for the inclusion of metallic salts [4.2]. Ion doped organic polymers are highly efficient in holographic recording [4.3].

The preparation of our photopolymer starts preparing aqueous solutions for every component using bi-distilled water. The solution composition for each component correspond to PVA (7% wt/wt), PDC (10% wt/wt) and Ni⁺² (10% wt/wt). They are defined in previous investigations [4.2].

The aqueous solution of PVA is prepared dissolving the powder heating without exceeding 60°. The powder is dissolved to get a uniform density and viscosity for smooth PVA solution. PDC and Ni⁺² solutions are mixed in a magnetic stirrer during 45 min to dissolve powder or crystals and they are heated for 5 min at the beginning. The final mixture is stirred and mixed well for 45 min to obtain a homogeneous coating solution. All the coating solution contains glycerol (40 µl).

The volume ratio of photosensitive solution is prepared depending on the study carried out to achieve the objectives. The evolution of diffraction efficiency as a function of composition's films is considered for this classification in table 4.2, which is studied in chapter 5.

Table 4.2 Classification of sample by composition's films.

Sample	Volume Ratio (ml)	Components
I	1:6:1	PDC:PVA:Ni
II	1:6	PDC:PVA
III	1:6:1.5	PDC:PVA:Ni

The photopolymer solution is deposited on the clean leveled substrate to form a solid plastic film which represents the holographic recording material. In our research project we use two kinds of substrate as shown in table 4.3.

Table 4.3 Substrates used to films.

Substrate	Trademark
Glass	Lauka Mexicana S.A. de C.V.
Commercial Transparency Films	3M-PP2900™

The glass substrate used in the experiments has a thickness between 1mm to 1.2mm and the area of the plates is 1456mm² [4.1, 4.4]. The commercial transparency film has an area of 1444mm². The quantity of coating solution to form the film is determined by the desired thickness of the photosensitive layer as observed in table 4.3. This classification is considered for the study of diffraction efficiency evolution as a function of thickness's films studied in chapter 5.

Table 4.4 Classification of sample by thickness's films.

Sample	Thickness (μm)	Volume of coating solution (μl)
A	34 \pm 1	40 \pm 1
B	75 \pm 1	80 \pm 1
C	105 \pm 1	120 \pm 1

After deposition of coating solution on the substrate a cover should be placed above the plate to prevent dust particles falling on the film. The coating solution is dried by gravity settling method. The drying time for the photosensitive layers is approximately 24 h (sample A) or 48 h (samples B and C). The thickness film is measured by Digimatic Micrometer (Mitutoyo Corporation[®], Model IP65).

The photosensitive layers used as recording media are derived from a combination of composition and thickness of coating solution as shown in table 4.5. In the chapter 5 we only present the results more significant.

Table 4.5 Classification of sample of photosensitive film.

Samples	I	II	III
A	IA	IIA	IIIA
B	IB	IIB	IIIB
C	IC	IIC	IIIC

The presence of water and PVA in the composition of the material and the way it is prepared have a decisive effect on the characteristics of the material. The initial solution is prepared when the material becomes a solid film and it is considered “dry”, water is continuously evaporated. When the holographic processing takes place, the material continues to exchange water with the atmosphere. The rate of evaporation depends on the relative humidity and this has a direct effect on the drying time and formation of the solid film. [4.5]

The optimum time to develop the plates is when they are just dry enough to be handled. Variations in drying time also affect the maximum diffraction efficiency reached. A lower concentration of water in the “dry” layer hinders the movement of molecules of the species in solution and reduces the diffusion coefficients; this has a great effect on the energetic sensitivity, since the rate of polymerization is reduced. If the concentration of water in the “dry” layer decreases far below the optimum value, there is also an excessive increase in the concentration of monomer, radical generator and dye; this implies low diffraction efficiency and the presence of strange peaks and other alterations on the exposure curves. [4.5]

Polymer plates with photosensitizer, once dried, they act like little sponges, and they immediately begin to absorb humidity of the environment. So, when the plates are dry usually working with them at that time.

The photosensitive layers are sandwiched between the substrates covers and between them there are two copper electrodes. The electrodes through to the emulsion are oriented perpendicular to the grooves, which were formed by the interference pattern.

The preparation of coating solution and films was made at room conditions in the laboratory. The range of room conditions for relative humidity is 42-62% and for temperature is 18-24°C [4.1].

4.1.1 Polyvinyl alcohol matrix

The commercial PVA is classified according to their molecular weight and degree of hydrolysis, which are the factors that determine the viscosity of the prepared solutions

and the capacity of polymers to retain water [4.5]. The main grades of polyvinyl alcohol can be classified as much hydrolyzed (97.5 – 99.5 %) and partially hydrolyzed (87 – 89 %) [4.2]. The average molecular weight of the commercial PVA can vary to between 20,000 and 200,000 [4.5]:

- PVA with a low average molecular weight have short chains and give solutions of low viscosity and little capacity to retain water per unit of mass.
- PVA with a high average molecular weight usually have very long polymer chains and when dissolved in water give solutions of high viscosity with a great capacity per unit of mass to retain water.

The choice of PVA is a fundamental factor in obtaining a material of great thickness. The PVA used normally in the bibliography for the study of photopolymers has a low molecular weight ($M_w = 27,000$). This is not suitable to obtain very thick layers capable of being used in holographic memories, which means that a high concentration is necessary and this hinders the photopolymerization process. Moreover, a great deal of solution must be deposited in order to obtain the required thickness, and given the small amount of water retained, the concentration of active substances in the dry film increases excessively. This gives rise to poor photopolymerization results, since this process depends directly on the concentrations in the film of material and not on the concentrations in the initial solution. [4.5]

On the other hand, a PVA with a high molecular weight has very long polymer chains which give rise to a high light dispersion. This is a factor to be borne in mind in the

process of recording and reading the data stored in the material. Consequently, it is necessary to find a type of PVA that allows sufficient water to be retained so as to obtain layers of the required thickness, and has a molecular weight such that the material does not exhibit excessive dispersion of light. [4.5]

PVA films doped with Cr^{+6} and Fe^{+3} are excellent in real time holographic recording materials [4.6]. The ion exchange is based on the distribution of soluble ions between an aqueous solution and a reactive polymer containing selective ligands [4.7].

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Chapter 5

Holographic gratings on dichromated polyvinyl alcohol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ doped films

Photopolymerizable materials belong to self-developed holographic materials and ensure simultaneous real-time writing and reading of holograms [5.1]. Interference recording of two shortwave in a holographic media modifies some of the optical properties of materials as conductivity and refraction index [5.2].

This chapter discusses the experimental process to record holographic gratings and the optical setup description to meet objectives. The experimental results are explained by the diffraction efficiency as a function of voltage, thickness, spatial frequency and relative humidity.

5.1 Optical setup

When polymeric materials like PVA is exposed to light it develop charged species (Table 4.2), and this species can migrate with electric field and thus conduct electricity. A self-diffraction was observed without applying a dc voltage under low intensity optical irradiation, but the first-order diffraction efficiency increased and the response time of the grating decreased with dc voltage [5.3].

The optical symmetrical setup to record the holographic gratings and read the diffraction intensity at the same time is showed in figure 5.1 and its description are explained as follows [5.4, 5.5]:

The film is exposed to recording laser beam “LR” of He-Cd (CVI Melles Griot[®], 50 mW, $\lambda = 442$ nm) which is moderately attenuated by a filter “F”, and is divided into two beams “IR1” and “IR2”, by a beam splitter “BS”. The mirrors “M1” and “M2” are used to direct respective beams on the sample, producing interference between them. The interfering beams cause modulation of refractive index. The diffracted light is measured simultaneously during recording by a He-Ne laser “Lr” (CVI Melles Griot[®], 30 mW, $\lambda = 632.8$ nm). The intensity of the diffracted beam “Ir(+1)” is measured at first order by a detector “D”. The light beam “Ir” from the “Lr” laser impacts on the sample and the light that is not diffracted corresponds to “Ir(0)”.

The diffracted beam is measured during hologram formation as a function of exposure time, although diffraction efficiency is reported as a function of exposure energy. The power supply, VR (B&K Precision Corp., USA) is connected to the sample [5.4] and the DC voltage is regulated until desired value (10, 20 and 30 V).

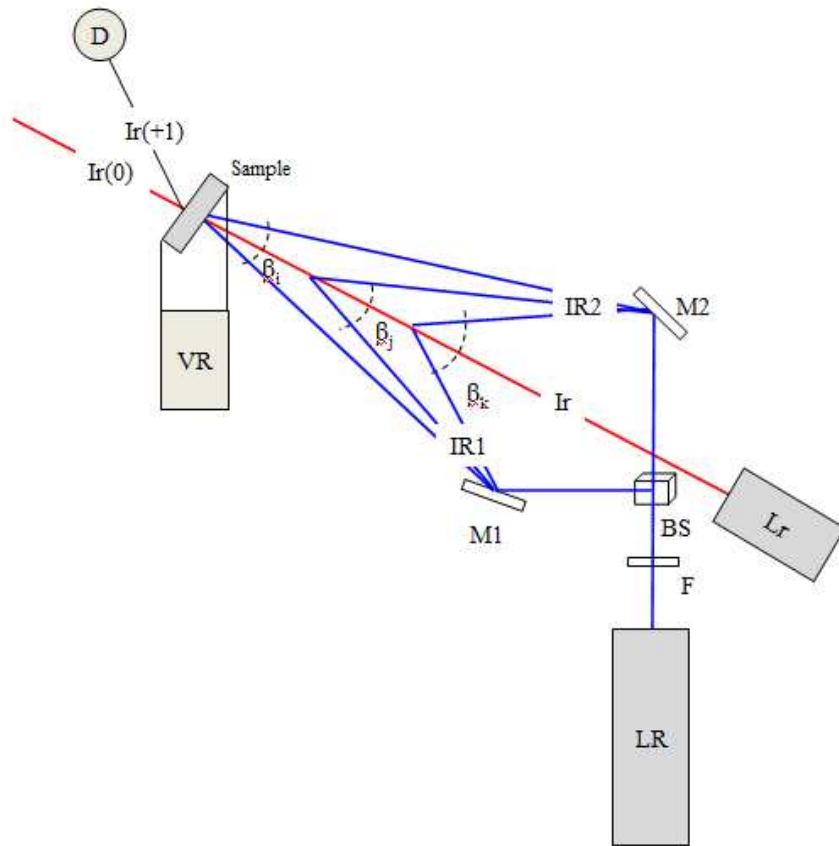


Figure 5.1 Optical setup for real-time holographic gratings recording by different spatial frequencies.

The experiment tests are carried out with and without voltage by different spatial frequencies and types of coating solutions which are function of thickness and composition materials. The angles of two intersecting recording beams are shown in table 5.1 are nonlinear and each angle corresponds to particular spatial frequency and period of gratings for the seven positions where samples are taken.

Table 5.1 Angles of intersecting recording beam and spatial frequency. [5.4]

	Angle	Spatial Frequency (lines/mm)	Period (μm)
β_1	24.3°	666	1.50
β_2	26.6°	726	1.38
β_3	28.1°	766	1.31
β_4	30.0°	816	1.23
β_5	32.3°	878	1.14
β_6	36.1°	978	1.02
β_7	40.6°	1098	0.91

The experimental setup illustrated in figure 5.1 describes seven angles that vary from β_1 to β_7 , and their values depend on the photosensitive plate position and intersecting recording beams. The angle increases as the film approaches the beam splitter. Photosensitive plate films are placed in these seven equally spaced positions, coming toward the beam splitter prism, to the closest position, number seven. Due to the physical size of the mechanical base that supports the photosensitive substrate, these seven measurements are made at constant distances. This behavior is purely circumstantial, due to the experimental methodology used, but this way of reporting the results does not alter the main context of what we want to describe. [5.4]

The diffraction efficiency curves are developed from the estimation of average values for experimental data that corresponds to some sets of recordings for different spatial frequency, thickness and composition samples, depending on the study reported.

The diffraction efficiencies are calculated at first order, and their values are normalized. The curves are defined by polynomial trend line for obtain more adequate visualization experimental results, and have a mathematical representation of the behavior of the material for future research.

5.1.1 Evolution of diffraction efficiency by relative humidity influence

The presence of external electron donors [5.6] and the effect of environmental humidity on the photosensitivity and the real time hologram recording had been investigated in dichromated polyvinyl alcohol (DCPVA) films [5.7].

The optimal time is determined mainly by external circumstances as environmental humidity, temperature, and laser beam stabilization, calibration of the radiometer, correct alignment of the holographic interferometric arrangement, and proper alignment of polarization of the beams.

The first parameter to be diminished affected is the energetic sensitivity, while the maximum diffraction efficiency is also reduced too long after the optimum point. [5.8]. The dependence of real time diffraction efficiency of DCPVA films on the relative environmental humidity has been studied for volume transmission holograms [5.7].

In order to achieve greater reproducibility and better results for the holographic parameters, the exact optimum processing point should be determined and the drying conditions (relative humidity and temperature) which must be strictly controlled [5.8].

In almost all cases studied, higher relative humidity has a positive effect on the photoreduction and the subsequent crosslinking in the PVA matrix; therefore, this notably improves the photospeed and the real time diffraction efficiency with and without electron donors; and low humidity environmental weakness its shelf life and reduces the diffraction efficiency several times [5.7].

Table 5.2 describes environmental conditions, pH of coating solution and spatial frequency to testing. The holographic properties of DCPVANI (sample IA) have been studied during real time holographic recording and the diffraction efficiency is estimated to order +1.

Table 5.2 Environmental conditions according to spatial frequency.

	Spatial Frequency (Lines/mm)			
	666		766	
Temperature (°C)	23.4	23.9	21.0	20.0
Relative Humidity (%)	42	54	62	44
pH	4.86	4.85	4.88	4.84

The holographic curve for the photosensitive films is a function of exposure energy. Figure 5.2(a) presents relative humidity of 42% and temperature of 23.4°C. Figure 5.2(b)

shows relative humidity of 54% and temperature of 23.9°C. The curves shows significantly changes of diffraction efficiency due voltage.

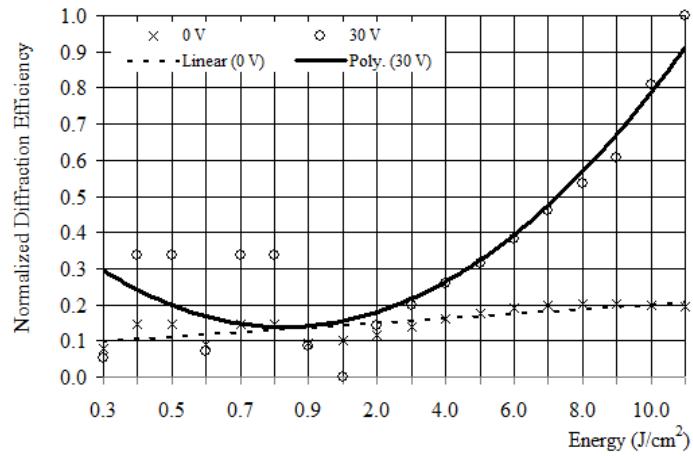
Table 5.3 describes the maximum diffraction efficiency (η_{\max}) value used in figure 5.2 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

Table 5.3 Maximum diffraction efficiency as reference to normalize the results in figure 5.2

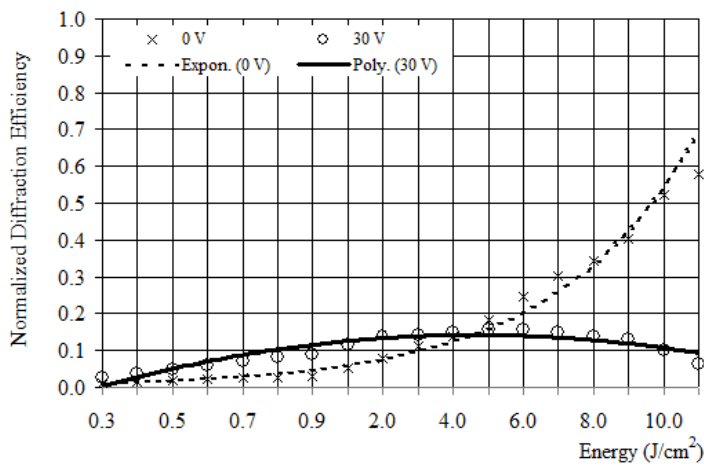
η_{\max}	Figure 5.2		Equations
3.342 %	(a)	0 V	$y = 0.0064x + 0.0905$
		30 V	$Y = 0.0056x^2 - 0.0706x + 0.3599$
	(b)	0 V	$y = 0.0081e^{0.2473x}$
		30 V	$Y = -0.0012x^2 + 0.0286x - 0.0243$

y: Normalized diffraction efficiency; x: Energy (J/cm²)

The best diffraction efficiencies are achieved when the experiment is carried out with voltage and low relative humidity as shown in figure 5.2(a). Environmental humidity modifies holographic curve performance, because the material absorbs the humidity, making the diffraction efficiency decreases with voltage in figure 5.2(b).



(a)



(b)

Figure 5.2 Normalized diffraction efficiency at spatial frequency of 666 lines/mm for two different relative humidities: (a) 42% and (b) 54%. [5.9]

Table 5.4 describes the maximum diffraction efficiency (η_{max}) value used in figure 5.3 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

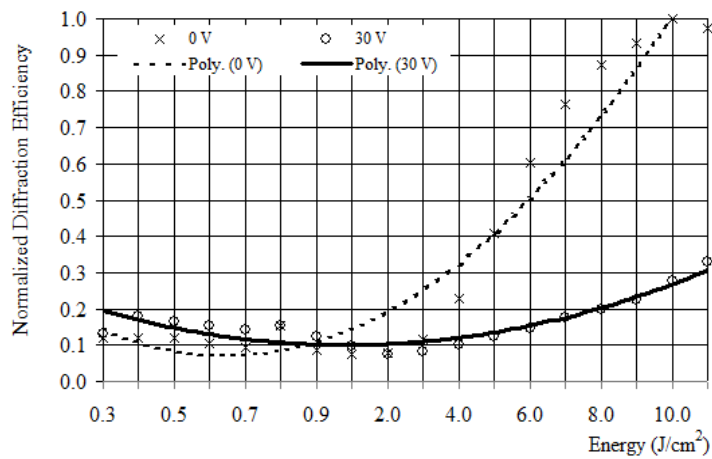
Table 5.4 Maximum diffraction efficiency as reference to normalize the results in figure 5.3.

η_{\max}	Figure 5.3		Equations
1.353 %	(a)	0 V	$y = 0.006x^2 - 0.0543x + 0.1928$
		30 V	$y = 0.002x^2 - 0.0313x + 0.2235$
	(b)	0 V	$Y = -0.0024x^2 + 0.021x + 0.6549$
		30 V	$y = 0.1004e^{0.1074x}$

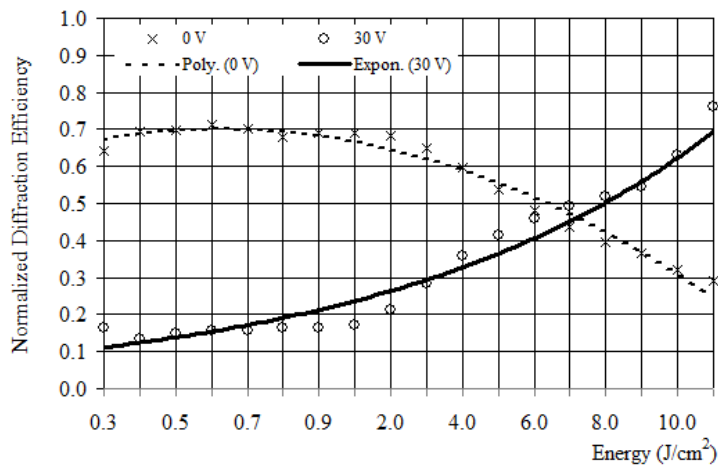
y: Normalized diffraction efficiency; x: Energy (J/cm^2)

Figure 5.3(a) presents relative humidity of 62% and temperature of 21.0°C. Figure 5.3(b) shows relative humidity of 44% and temperature of 20.0°C. Both curves present a meaningful modulation of diffraction efficiency when it is applied a voltage. The saturation to holographic curve without voltage is achieved during this exposure energy while for the voltage curve is necessary more exposure energy to observe the maximum value of diffraction efficiency.

Higher environmental humidity of 62% as in figure 5.3(a) shows the maximum diffraction efficiency reached without voltage to spatial frequency of $f_3 = 766$ lines/mm, although lower environmental humidity of 44% as in figure 5.3(b) exhibits the maximum diffraction efficiency with voltage.



(a)



(b)

Figure 5.3 Normalized diffraction efficiency at spatial frequency of 766 lines/mm by two different relative humidities: (a) 62% and (b) 44%. [5.9]

Diffraction efficiency and energetic sensibility to real time holographic recording are influenced by environmental humidity conditions; they depend on the nature of the photosensitive material and the spatial frequency to holographic recording even if there is or not voltage presence [5.9].

5.1.2 Evolution of diffraction efficiency by module transfer function

The module transfer function (MTF) of the material could make possible the prediction and optimization of the quality of the holographic image [5.10-5.12]; as well the spatial frequency of imaging system can be described by MTF [5.13].

This parameter is commonly used in optical imaging, and determines the optical system's ability to resolve every detail of the object, represented by spatial frequencies; this is called transfer function TF. To view the TF is measured by units of intensity normalized MTF. Similarly, the parameter of holographic diffraction efficiency, which corresponds to a normalization of intensities, we apply the same concept.

MTF curves for normalized diffraction efficiency as a function of spatial frequency to photosensitive material is plotted in figure 5.4. For this study we considerer all the seven spatial frequency reported in table 5.1. There is an alteration (modulation) which reflects an increase of ability to redirect its molecular structure through an affluent of free electrons supplied by the metal salts of nickel chloride; this induces a kind of latent image amplification by free charges which are reflected as a higher refractive index modulation when it is exposed to blue light of He-Cd [5.4].

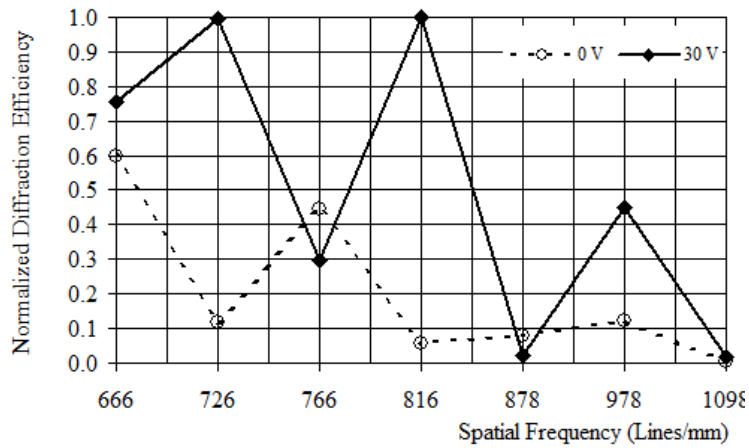


Figure 5.4 MTF curve of holographic gratings on DCPVANI films [5.4].

Contrast and brightness of image decrease when the spatial frequency increases its value and diffraction efficiency increases when the voltage is applied during hologram formation to photosensitive layer [5.4]. The best normalized diffraction efficiency value observed with voltage corresponds to spatial frequency of $f_2 = 726$ and $f_4 = 816$ lines/mm. In the case without voltage the top of normalized diffraction efficiency is obtained to $f_1 = 666$ lines/mm. The maximum diffraction efficiency (η_{\max}) value used as a reference to normalize the diffraction efficiencies results is 2.007%.

The image quality of holographic gratings on this photopolymer material is better at low spatial frequency that is due to the natural answer of the spatial modulation of the polymeric material, which it is not lineal, like in many materials [5.4]. Table 5.5 describes the changes on diffraction efficiency due to voltage and the greatest region to use for recording.

Table 5.5 Modulation of diffraction efficiency as a function of MTF.

<i>F</i> (lines/mm)	η (%)		$\Delta\eta$ (%)
	0 V	30 V	
666	1.204	1.520	0.316
726	0.235	1.998	1.763
766	0.894	0.592	-0.302
816	0.115	2.007	1.892
878	0.154	0.047	-0.107
978	0.246	0.902	0.656
1098	0.011	0.039	0.028

The diffraction efficiency and imaging quality of volume holographic gratings of DCPVANI films (sample IA) are determined by different spatial frequencies and voltage [5.4].

5.1.3 Evolution of diffraction efficiency as a function of thickness and spatial frequency

Diffraction efficiency during holographic gratings formation on DCPVANI layer (sample I) is studied with and without voltage, for three types of samples which depending on the film thickness: 34 μm (A), 75 μm (B) and 105 μm (C). The spatial frequency used in this experiment is $f_2 = 726$ lines/mm.

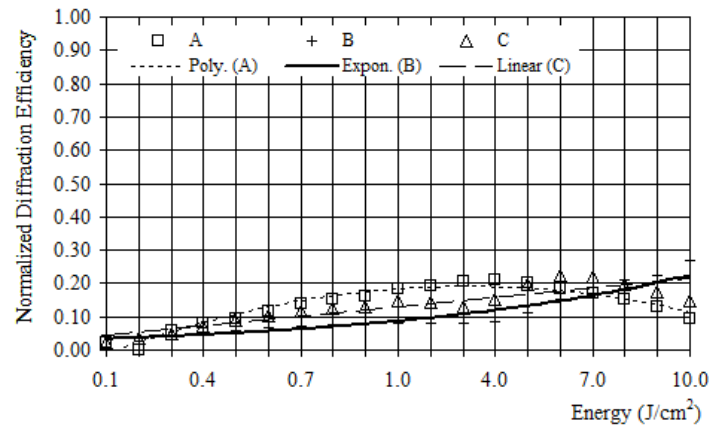
Table 5.6 describes the maximum diffraction efficiency (η_{\max}) value used in figure 5.5 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

Table 5.6 Maximum diffraction efficiency as reference to normalize the results in figure 5.5.

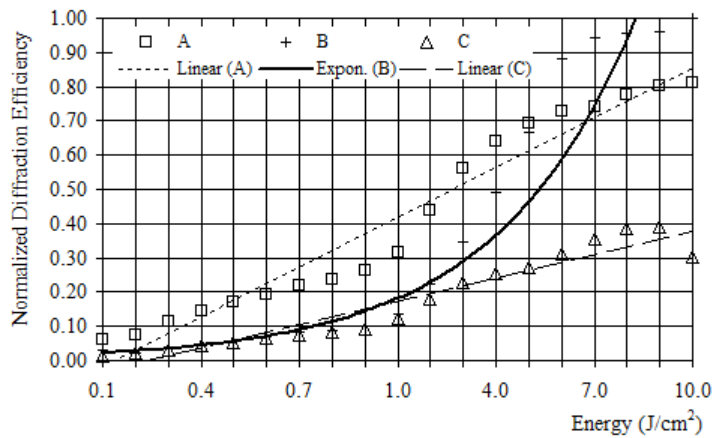
η_{\max}	Figure 5.5		Equations
2.469 %	(a)	A	$y = -0.0016x^2 + 0.0399x - 0.0505$
		B	$y = 0.0301e^{0.1061x}$
		C	$y = 0.0093x + 0.0375$
	(b)	A	$y = 0.0485x - 0.065$
		B	$y = 0.0175e^{0.2343x}$
		C	$y = 0.0227x - 0.0541$

y: Normalized diffraction efficiency; x: Energy (J/cm^2)

Evolution of diffraction efficiency without voltage, as a function of exposure's energy, is shown in figure 5.5(a). The normalized diffraction efficiency reaches the saturation peak to $4 J/cm^2$ and $6 J/cm^2$ for curves A and C, respectively. The curve B continues increasing without to get the saturation and the maximum normalized diffraction efficiency is obtained to $10 J/cm^2$ [5.5].



(a)



(b)

Figure 5.5 Evolution of diffraction efficiency for different thicknesses to 726 lines/mm - Sample I: (a) 0 V and (b) 30 V

Generally, the curves increase quickly with voltage and the values are bigger than without voltage, which represents a significant modulation of diffraction efficiency. Figure 5.5(b) shows the evolution of diffraction efficiency as a function of exposure's energy with voltage. The highest values of normalized diffraction efficiency are reached to 9 J/cm², for samples A and B, and to 8 J/cm², for sample C [5.5].

The development of diffraction efficiency curves for three different thickness films is determined with or without voltage but in both cases the sample IB has the most favorable thickness to register holographic gratings for this exposure energy at $f_2 = 726$ lines/mm and the greatest values of diffraction efficiency take place with voltage [5.5].

These types of emulsions usually do not present diffraction efficiencies as high as conventional holograms display due to duality answer: the ability to record holographic images and the potential response with voltage to low intensity; this opens new opportunities to innovation diffractive optical elements development which can be modulated by a voltage signal [5.5].

Real time holographic recording on photosensitive layer I is also studied varying the thickness and spatial frequency in addition to with and without voltage. The thicknesses of film are $34 \mu\text{m}$ (A), $75 \mu\text{m}$ (B) and $105 \mu\text{m}$ (C). The spatial frequency study is defined for $f_2 = 726$ lines/mm, $f_3 = 766$ lines/mm, $f_5 = 878$ lines/mm and $f_6 = 978$ lines/mm.

Table 5.7 describes the maximum diffraction efficiency (η_{max}) value used in figure 5.6 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

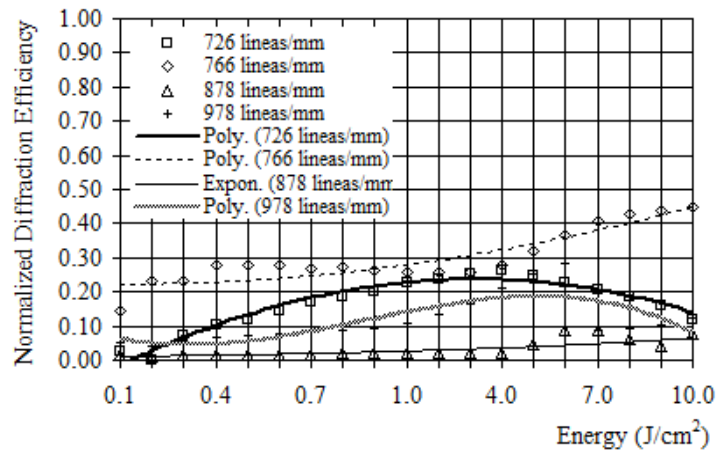
Table 5.7 Maximum diffraction efficiency as reference to normalize the results in figure 5.6.

η_{\max}	Figure 5.6		Equations
1.998 %	(a)	726 lines/mm	$y = -0.002x^2 + 0.0493x - 0.0624$
		766 lines/mm	$y = 0.0007x^2 - 0.0017x + 0.2241$
		878 lines/mm	$y = 0.01e^{0.0984x}$
		978 lines/mm	$y = -0.0002x^3 + 0.0055x^2 - 0.0284x + 0.0864$
	(b)	726 lines/mm	$y = 0.0599x - 0.0803$
		766 lines/mm	$y = 0.0002x^3 - 0.0042x^2 + 0.0257x + 0.1349$
		878 lines/mm	$y = -0.0001x^3 + 0.003x^2 - 0.0197x + 0.05$
		978 lines/mm	$y = 0.0239e^{0.1388x}$

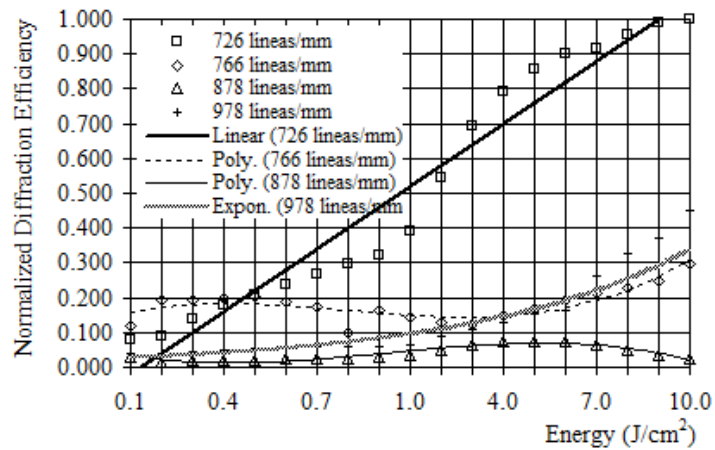
y: Normalized diffraction efficiency; x: Energy (J/cm^2)

Figure 5.6 shows two graphics, with and without voltage, with evolution of diffraction efficiency in sample IA to different spatial frequency. The maximum value of normalized diffraction efficiency without voltage is reached to $10 J/cm^2$ which corresponds to $f_3 = 766$ lines/mm as shown in figure 5.6(a) and with voltage it is also reached to $10 J/cm^2$ to $f_2 = 726$ lines/mm as presented in figure 5.7(b).

The diffraction efficiency evolution with voltage improves respect to without voltage results. The diffraction gratings with voltage have more sensibility than without voltage due to the fact that it produces a significant faster time of response and rate of photo-polymerization.



(a)



(b)

Figure 5.6 Normalized diffraction efficiency for spatial frequency profile - Sample IA: (a) 0 V and (b) 30 V

The evolution of diffraction efficiency getting in sample IB is obtained by different spatial frequency allow identify what is the optimum position to get the best diffraction efficiency as a function of exposure energy with this conditions.

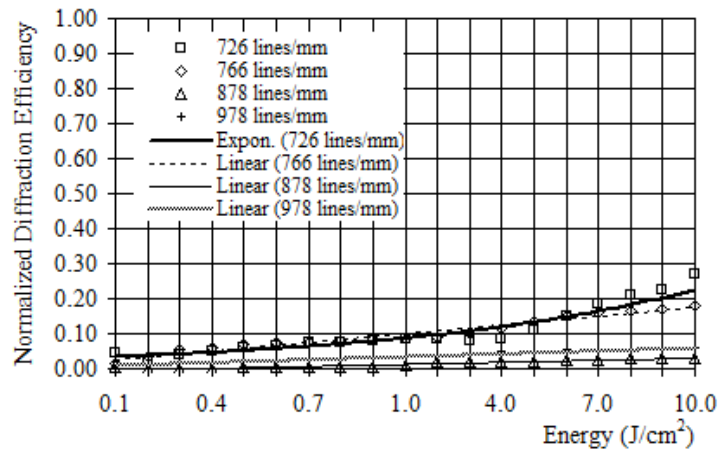
Table 5.8 describes the maximum diffraction efficiency (η_{\max}) value used in figure 5.7 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

Table 5.8 Maximum diffraction efficiency as reference to normalize the results in figure 5.7.

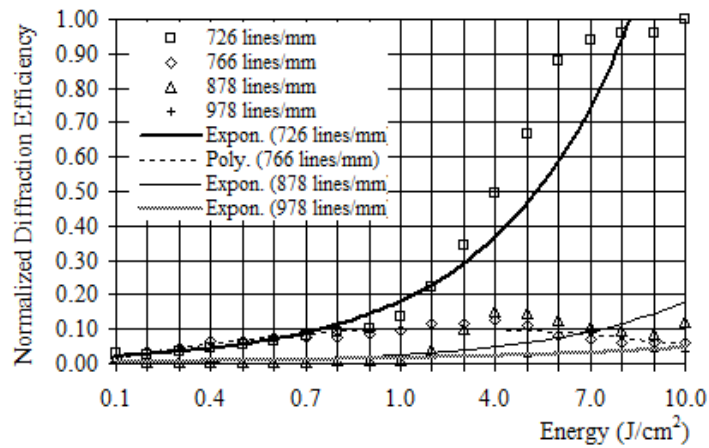
η_{\max}	Figure 5.7		Equations
2.469 %	(a)	726 lines/mm	$y = 0.0301e^{0.1061x}$
		766 lines/mm	$y = 0.0082x + 0.018$
		878 lines/mm	$y = 0.0018x - 0.0045$
		978 lines/mm	$y = 0.0029x + 0.0075$
	(b)	726 lines/mm	$y = 0.0175e^{0.2343x}$
		766 lines/mm	$y = -0.0008x^2 + 0.0186x - 0.0033$
		878 lines/mm	$y = 0.003e^{0.2151x}$
		978 lines/mm	$y = 0.0049e^{0.117x}$

y: Normalized diffraction efficiency; x: Energy (J/cm^2)

The greatest diffraction efficiency reached for this sample corresponds to $f_2 = 726$ lines/mm either with voltage for figure 5.7(a) or without it for figure 5.7(b). Maximum diffraction efficiency used to normalize the values corresponds to energy of $10 J/cm^2$ with voltage.



(a)



(b)

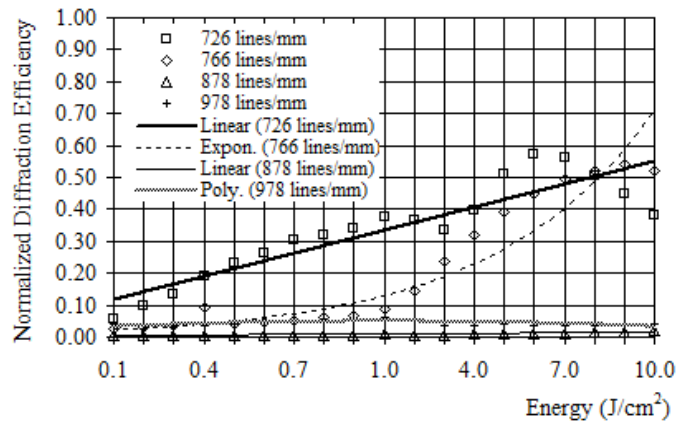
Figure 5.7 Normalized diffraction efficiency for spatial frequency profile - Sample IB: (a) 0 V and (b) 30 V

Progression of diffraction efficiency by different spatial frequency is considered in sample IC. Table 5.9 describes the maximum diffraction efficiency (η_{max}) value used in figure 5.8 as a reference to normalize the diffraction efficiencies results and the equations obtained due mathematical representation of trend line.

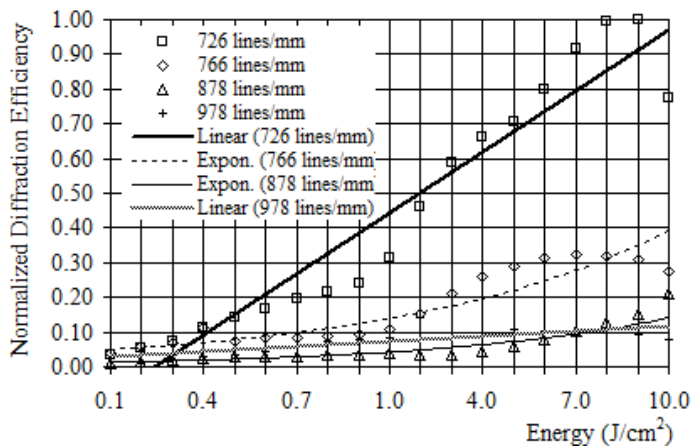
Table 5.9 Maximum diffraction efficiency as reference to normalize the results in figure 5.8.

η_{\max}	Figure 5.8		Equations
0.959 %	(a)	726 lines/mm	$y = 0.0239x + 0.0967$
		766 lines/mm	$y = 0.0195e^{0.1895x}$
		878 lines/mm	$y = 0.0006x + 0.0039$
		978 lines/mm	$Y = -0.0002x^2 + 0.004x + 0.0292$
	(b)	726 lines/mm	$y = 0.0584x - 0.1394$
		766 lines/mm	$y = 0.0441e^{0.1149x}$
		878 lines/mm	$y = 0.0114e^{0.1318x}$
		978 lines/mm	$y = 0.0048x + 0.0247$

y: Normalized diffraction efficiency; x: Energy (J/cm^2)



(a)



(b)

Figure 5.8 Normalized diffraction efficiency for spatial frequency profile - Sample IC: (a) 0 V and (b) 30 V

The upper limit of normalized diffraction efficiency corresponds to 10 J/cm^2 without voltage in figure 5.8(a) and 8 J/cm^2 with voltage in figure 5.8(b), both of them are gotten to $f_2 = 726 \text{ lines/mm}$.

From the experimental results, we can infer that the thickness is an important factor that influences the efficiency values. In this particular case, the sample IB shows the best qualities to spatial frequency at $f_2 = 726 \text{ lines/mm}$ for voltage test which increase significantly respect to with no voltage study.

5.1.4 Evolution of diffraction efficiency as a function of composition's films

Experimental data is developed at real time with and without voltage for three types of films which are a function of coating solution composition and volume ratio (samples I, II and III). The thickness considered in this experiment corresponds to sample B ($75 \mu\text{m}$) which presented the best diffraction efficiency results and the spatial frequency is $f_2 = 726 \text{ lines/mm}$.

Table 5.10 describes the maximum diffraction efficiency (η_{max}) value used as a reference to normalize the diffraction efficiencies results in figure 5.9 and the equations obtained due mathematical representation of trend line.

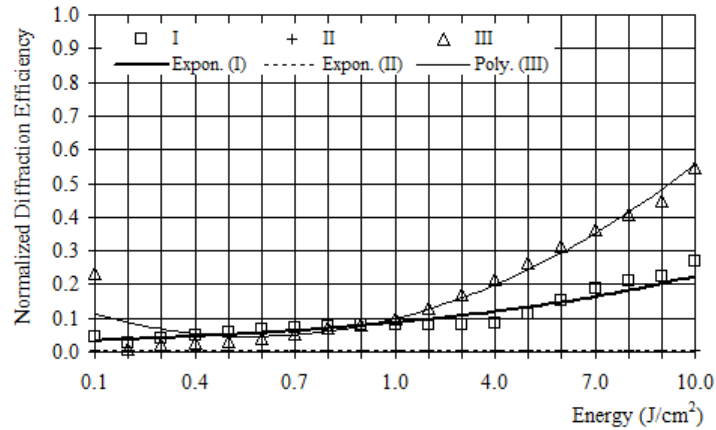
Table 5.10 Maximum diffraction efficiency as reference to normalize the results in figure 5.9.

η_{\max}	Figure 5.9		Equations
2.469 %	(a)	I	$y = 0.0301e^{0.1061x}$
		II	$y = 0.0027e^{0.0175x}$
		III	$y = 0.0029x^2 - 0.0332x + 0.1414$
	(b)	I	$y = 0.0175e^{0.2343x}$
		II	$y = 0.0066x - 0.0239$
		III	$y = 0.0446e^{0.1683x}$

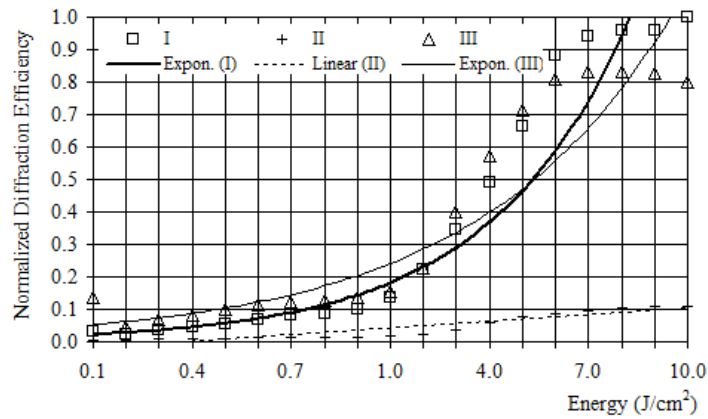
y: Normalized diffraction efficiency; x: Energy (J/cm^2)

Figure 5.9(a) gives an idea about the evolution of diffraction efficiency without voltage for films: I, II and III. The best diffraction efficiency behavior of curves corresponds to coating III which has more nickel in its solution composition; the maximum normalized diffraction efficiency takes place to $10 J/cm^2$. The curve for film II is insignificant respect the other two curves due this film does not have metallic salt in the coating solution, that is an evidence of positive effect of nickel in the solution.

Figure 5.9(b) illustrates the evolution of diffraction efficiency with voltage (30V) for films: I, II and III. The values increase a lot with voltage and the curves get the saturation. The highest normalized diffraction efficiency corresponds to coating I at $10 J/cm^2$. The curve for film II for voltage remains insignificant respect the other two but increase relatively to absent of voltage. Then, it can be conclude that voltage increase the diffraction efficiency for this films under this conditions of thickness and spatial frequency.



(a)



(b)

Figure 5.9 Evolution of normalized diffraction efficiency for different coating solution. Thickness: 75 μm and Spatial frequency: 726 lines/mm. (a) 0 V and (b) 30 V

5.1.5 Evolution of diffraction efficiency with change of voltage

The study of diffraction efficiency using different voltages is carried out at $f_0 = 978$ lines/mm for sample IA. The results are shown in figure 5.10, which can observe that diffraction efficiencies with 30 V are higher than those with 10 and 20 V. In the above figures, we have been discussed that in most of the cases the voltage has a positive effect

for the increase of diffraction efficiency but from this test we can infer that the voltage has to be significantly high to make the difference in the results.

Table 5.11 describes the maximum diffraction efficiency (η_{\max}) value used as a reference to normalize the diffraction efficiencies results in figure 5.10 and the equations obtained due mathematical representation of trend line.

Table 5.11 Maximum diffraction efficiency as reference to normalize the results in figure 5.10.

η_{\max}	Figure 5.10	Equations
0.902 %	10 V	$y = 0.0024x + 0.0085$
	20 V	$y = 0.0022x + 0.0197$
	30 V	$y = 0.053e^{0.1388x}$

y: Normalized diffraction efficiency; x: Energy (J/cm^2)

The curve for 0 V is notably higher than curves with 10 and 20 V but significantly lower than curve of 30 V, where the latest curve mentioned does not yet reach saturation.

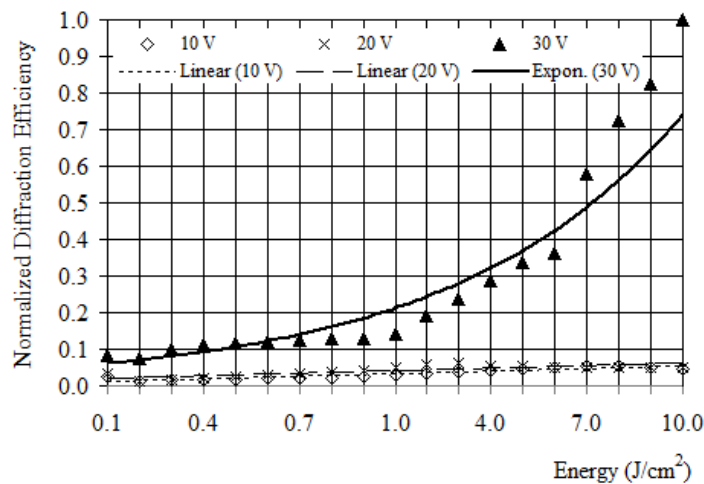


Figure 5.10 Evolution of normalized diffraction efficiency for sample IA by voltage changes. Thickness: 34 μm and Spatial frequency: 978 lines/mm.

5.1.6 Evolution of diffraction efficiency as a function of substrate

Table 5.12 describes the maximum diffraction efficiency (η_{\max}) value used as a reference to normalize the diffraction efficiencies results in figure 5.11 and the equations obtained due mathematical representation of trend line.

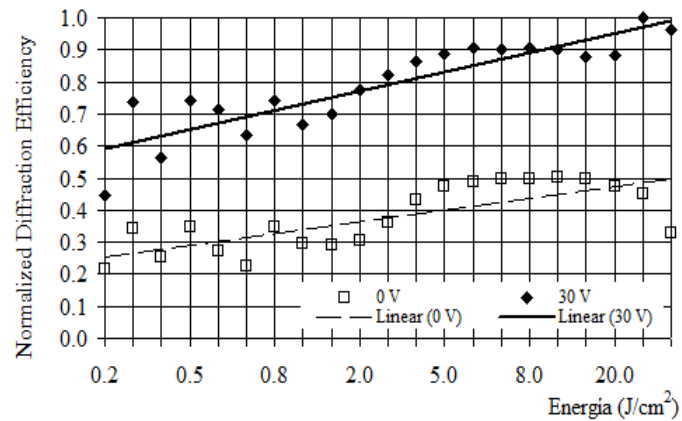
Table 5.12 Maximum diffraction efficiency as reference to normalize the results in figure 5.11.

η_{\max}	Figure 5.11		Equations
5.697 %	(a)	0 V	$y = 0.0121x + 0.2433$
		30 V	$y = 0.0199x + 0.573$
	(b)	0 V	$y = 0.0179e^{0.1214x}$
		30 V	$y = 0.0232e^{0.1428x}$

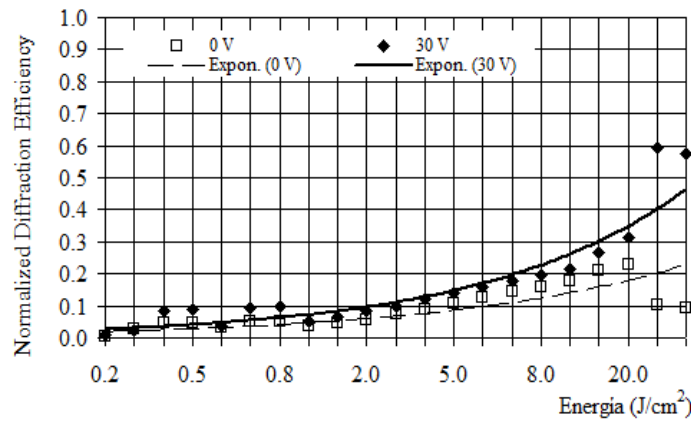
y: Normalized diffraction efficiency; x: Energy (J/cm^2)

The study is carried out at spatial frequency $f_l = 666$ lines/mm with sample IA. Figure 5.11(a) presents the holographic curve for commercial transparency film substrate with pH of 6 and room conditions of relative humidity and temperature of 32% and 19.3 °C, respectively. Figure 5.11(b) presents the holographic curve for glass substrate with room humidity of 46%, temperature of 23.6 °C and pH of 5.

Both figures, the holographic curve without voltage reaches the saturation, and after that the diffracted intensity starts to decrease. The holographic curve with voltage grows up when the exposure energy increases.



(a)



(b)

Figure 5.11 Normalized diffraction efficiencies of hologram formation with different substrates: (a) Commercial transparency film substrate, and (b) Glass.

The maximum values of normalized diffraction efficiencies achieved are observed in figure 5.11(a) when the commercial transparency film is used as substrate. The better experimental results about diffraction efficiencies correspond to commercial transparency at this spatial frequency and environmental conditions. The photosensitive material shows a significant dependence of the substrate, factor pH and relative humidity to evolution of diffraction efficiency.

5.2 Sensitivity of DCPVANI film

Table 5.13 shows the sensitivity of the material studied for sample IA considering the voltage modulation and using the results based on figure 5.6 where the best sensitivity takes place for 816 lines/mm with ad without voltage. The maximum angular sensitivity corresponds to 666 lines/mm.

Table 5.13 Sensitivity and angular sensitivity of DCPVANI ($d = 34 \mu\text{m}$) as a function of spatial frequencies.

f (lines/mm)	θ	0 V		30 V	
		η (%)	S (cm/J)	η (%)	S (cm/J)
666	0.44	1.204	3.227	1.520	3.626
726	0.41	0.524	5.323	1.998	4.157
816	0.36	0.206	33.373	2.007	4.167
978	0.30	0.563	3.678	0.902	2.793

Table 5.14 illustrates the sensitivity of the material studied for sample I taking into consideration the voltage modulation and thickness for results of figure 5.5 where the best sensitivity values corresponds to thickness A ($d = 34 \pm 1 \mu\text{m}$) with ad without voltage.

Table 5.14 Sensitivity of DCPVANI ($f_2 = 726$ lines/mm) as a function of thickness.

d (μm)	0 V		30 V	
	η (%)	S (cm/J)	η (%)	S (cm/J)
34 ± 1	0.524	5.323	1.998	4.157
75 ± 1	0.663	1.809	2.469	2.095
105 ± 1	0.551	0.707	0.959	1.036

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Chapter 6

Discussion

- The photosensitive material (PVA doped with dichromate and nickel) is developed as an alternative photopolymer for recording media. The use of nickel as sensitizer improves the optical results in diffraction efficiency. The additional wet chemical developing process is not needed.
- The holographic gratings are already analyzed during the exposition process and hologram formation can be detected immediately after exposure and hence the polymerization process. The environmental conditions and pH of solution really affect the performance of material to holographic formation.
- The results of holographic gratings are studied for diverse parameters as spatial frequency, thickness and composition of coating solution, but we always differentiate between with and without voltage application.
- The light exposure to this photosensitive material develops charged species, and this species can migrate under an electric field and thus conduct electricity. This behavior is taken advantage of addition of nickel chloride and voltage, which fundamentally increase the diffraction efficiency. The electronic orientation also contributes with this improvement because the flow of free electrons guided along

the grooves forms of the diffraction gratings. The photoinduced electron transfer processes caused by excited electronic states of compounds has an effect of strengthen in the modulation of the diffraction gratings due to the free radicals get excitation with luminous radiation of recording beam, and it is form part of fundamental properties of the materials.

- The diffraction efficiency values are normalized respect the maximum value in each figure and the curves are defined by polynomial trend line. These experimental results are modest, but their contribution is focused to positive voltage effect over the performance, which give us an idea about the feasibility of this material to duality of behavior: photosensitivity and ability to conduct electricity. The potassium dichromate and nickel chloride allow that both duality persist it is an important accomplishment owing to the nature of chromium which generally oxidizes tightly surrounding components. The nickel chloride hexahydrate agree to an easy assimilation into the polymeric matrix (PVA) due extra water content, which is used to make a conductive film.
- The fact that diffraction devices can census information for small electric fields this material becomes attractive for technological performance idea. This photosensitive material can be used to develop holographic devices for areas such as MOEMS and MEMS, after some parameters are optimized.

This line of investigation can be continuing grow up, especially in the enhancement of this photopolymer material as recording media. It could be taking advantage of its

photosensitivity and ability as conductor media. Then the future investigations would include:

- Increase the efficiency of holographic diffraction gratings in this material by the insertion of various polymeric matrices.
- Increase the voltage response range of this material.
- Perform the signal modulations through this material.
- Study the behavior of the resistivity, conductivity, charge transport, charge density of this material.
- Increase the stability of this material hygroscopic and the lifetime of recorded gratings.
- Implement the development of electro-optical devices using this material.

Chapter 7

Conclusions

The main conclusions resulting of the study of behavior of holographic gratings as a function of voltage on dichromated poly vinyl alcohol doped with nickel (II) chloride hexahydrate are enunciate as follows:

- The samples studied have a great capacity for modulation of the diffraction efficiencies of voltage application.
- The most modulation efficiencies holographic diffraction gratings is presented for DCPVANI film to 816 lines / mm ($\Delta\eta_{30V-0V} = 1.892\%$).
- The relative humidity affects the diffraction efficiencies with significant modulation response of the material where: $\eta_{30V} > \eta_{0V}$ when RH <50%.
- The use of Ni⁺² as sensitizing agent markedly improved diffraction efficiencies in dichromated polyvinyl alcohol.
- The best results of diffraction efficiency corresponds to thickness B ($d = 75 \pm 1 \mu\text{m}$) and spatial frequency $f_2 = 726$ lines/mm.

- The lower exposure energy required for holographic recording when voltage is applied corresponds to spatial frequency $f_d = 816$ lines/mm, thickness A ($d = 34 \pm 1$ μm) and sensitivity ($S = 4.167$ cm/J).
- The best results of diffraction efficiency as a function of substrate were obtained with the commercial transparency.

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1. **Fontanilla-Urdaneta, R.C.**, Olivares-Pérez, A. and Fuentes-Tapia, I., “Real-time holographic gratings modulate with voltage by different thickness film”, *Opt. Eng.* **50**(4), 045801.1-045801.3 (2011).
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3. **Fontanilla-Urdaneta, R.C.**, Olivares-Pérez, A., Fuentes-Tapia, I. and Ríos-Velasco, M.A., “Environmental conditions influence for real-time hologram formation on dichromated polyvinyl alcohol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ doped films”, *J. Phys.: Conf. Ser.* **274**(1), 012037 (2011).
4. **Fontanilla-Urdaneta, R. C.**, Olivares-Pérez, A., Fuentes-Tapia, I., Ríos-Velasco, M. A. “Study of pH effect and aging of coating emulsions for hologram recording.” Proceeding of SPIE. 7619-29 (2010).
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6. **Fontanilla-Urdaneta, R. C.**, Olivares-Pérez, A. and Fuentes-Tapia, I., “Holographic gratings doped with dichromate and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ”, Décimo Encuentro de Investigación INAOE, 2009.
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9. Páez-Trujillo, G., Olivares-Pérez, A., Mejias-Brizuela, N., Garay-Hernández, M. P., **Fontanilla-Urdaneta, R.**, Fuentes-Tapia, I., Toxqui-López, S., "Dichromated polyvinyl alcohol films doped with organic colorants" in *Practical Holography XXII: Materials and Applications*, edited by Hans I. Bjelkhagen, Raymond K. Kostuk, Proceedings of SPIE Vol. 6912 (SPIE, Bellingham, WA 2008) 691204.
10. Hernández-Garay, M. P., Olivares-Pérez, A., **Fontanilla-Urdaneta, R.**, Páez-Trujillo, G., Mejias-Brizuela, N., Fuentes-Tapia, I., "Optical properties of composite organic conductive films by holographic storage" in *Practical Holography XXII: Materials and Applications*, edited by Hans I. Bjelkhagen, Raymond K. Kostuk, Proceedings of SPIE Vol. 6912 (SPIE, Bellingham, WA 2008) 691205.
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 14. Páez-Trujillo, G., Olivares-Pérez, A., Mejias-Brizuela, N., Garay-Hernández, M. P., **Fontanilla-Urdaneta, R.**, Fuentes-Tapia, I., Amigón-De León, E., "Hologram with dichromated polyvinyl alcohol and natural colorant" in *Organic 3D Photonics Materials and Devices*, edited by Susanna Orlic, Klaus Meerholz, Proceedings of SPIE Vol. 6657 (SPIE, Bellingham, WA 2007) 66570N.
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