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Abstract. We propose the use of polyvinyl alcohol photosensitized with copper chloride dihydrated $CuCl_2(2H_2O)$ as a photosensitive material for recording holographic gratings. We obtained different dissolutions changing concentration of photosensitive agent and varying their *p*H factor, refraction index, and optical density for each sample. We registered diffraction gratings by holographic methods. The behaviors of diffraction efficiency parameters of holographic gratings regarding the concentration of a photosensitive agent were analyzed. We show there exists a correspondence between the diffraction efficiency parameter with concentration change of $CuCl_2(2H_2O)$. The low toxicity of this holographic recording material as well as its peculiar behavior, photosensitivity, and ability to conduct electricity, makes it attractive for production diffractive optical elements with bio-polymers. [DOI: 10.1117/1.3589293]

Subject terms: holography; holographic materials; holographic gratings.

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1 Introduction

Photopolymer materials are practical materials to use as holographic recording media—they are inexpensive and self-processing (dry processed).[1] Budkevich et al. presented one of the first works based on inorganic halide photolysis, with a halide dispersed in a rigid polymer, in this case polyvinyl alcohol (PVA) which governs changes in optical characteristics (refractive index, absorption coefficient, and surface relief).[2] Initiators for such modification were halides of iron (III), copper (II), titanium (IV), chromium (II), bismuth (III), and so on, which were introduced like simple salts and as coordination compounds.[3] Weiss et.al.[4] showed a technique to control gratings with anomalies in photoactive polymers. They formed gratings on acrylamide monomers, which were dissolved together with xanthenes dye in PVA. It was used with an agent to stabilize grating structures against dimensional distortions; this agent was $CuCl_2$ which is known as gelation agent with PVA solutions.[3] The addition of cross-linking agents significantly increased maximum diffraction efficiency at Bragg conditions. There are works about PVA with dichromate and with other metallic elements to form photopolymers,[1] however we have an interest to work with copper chloride dihydrate $CuCl_2$ $(2H_2O)$, because it shows an ability to be easily mixed with aqueous samples at environmental conditions. We have worked with this material and report some preliminary partial results.[5]

We presented a process of PVA prepared with $CuCl_2(2H_2O)$ as a photosensitive material for recording holographic gratings. We explore the capability of material regarding concentrations of $CuCl_2(2H_2O)$. We could see correspondence between *p*H, optical density, and refraction index of each sample. According to experimental developments there are relations between salt concentration and performance sample. This holographic recording material has low toxicity and makes it attractive for production of diffractive optical elements with bio-polymers.

The manuscript is organized as follows. In Sec. 2 we describe sample preparation and we report chemical characteristic of solution for different concentrations of $CuCl_2(2H_2O)$, as well as holographic register description, though the optical setup was used to make diffraction gratings. In Sec. 3 we present experimental results, explore diffraction efficiency as a function of chemical and physical characteristic of samples, exposure energy and register angle of gratings. The work ends with our conclusions in Sec. 4.

2 Experimental Development

2.1 *Samples Preparation*

The polymeric matrix used in this work for holographic recording is PVA (Meyer®). It is water soluble and has the ability of undergoing changes of crosslinking in its molecular structure[6] when it is irradiating with a thermal source. The synthesis of these photopolymer films starts preparing aqueous solutions for every component. Each solution is stirred and mixed for 45 min or more to dissolve the powder or

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crystals. In the process, the PVA solution is heated to 90°C and copper is mixed at room temperature. As a first step, we prepared the polymeric matrix in aqueous solution with 25% of PVA; this solution is called solution A (PVA + H_2O). On the other hand, aqueous solution B [$CuCl_2(2H_2O)$ + H_2O] is formed by 50% of $CuCl_2(2H_2O)$ (powder solution) regarding H_2O volume. Solutions A and B are base solutions in terms of weight–weight percentage (w/w %) to carry out the different aqueous concentrations that we proposed in this work. Preparation A + B has a total of 10 ml. These coating solutions also contain glycerol (1 μl); the mixture is stirred and mixed well to get a homogeneous solution. Every aqueous solution A and B to form concentration ratios were mixed with normal laboratory environment conditions of 19°C to 22°C and relative humidity of 30% H to 35% H.

The substrate used in this experiment is glass (Lauka®). The glass has a thickness of 1 ± 0.2 mm and the area of plates is 56 × 26 mm. The amount of solution poured on the substrate is 40 μl and it is determined like a function of desired thickness of sensitive layer. This process is realized with a hot substrate at 50°C. The photosensitive plate is left to cool slowly until gets to room temperature.

A gravity method has been adopted to obtain dried coatings. After deposition of the coating solution on a substrate, it is necessary to protect a photosensitive emulsion plate of dust particles falling on film drying time, between 24 to 36 h approximately.

The total thickness of the film is 200 μm and it is measured by Digimatic Micrometer (Mitutoyo Corporation®, Model IP65).

After testing different concentrations of PVA and $CuCl_2(2H_2O)$, we decided to make the following concentrations as showed in Table 1.

The characteristics of aqueous solutions, as *p*H parameter, was measured with a *p*H-meter (conductronics ph15®). This parameter is affected when concentrations of $CuCl_2(2H_2O)$ changes[7,8] and *p*H variation is a parameter that will be influenced in preparation of films for holographic register. In

Table 1 Solution A is PVA + H_2O and solution B is $CuCl_2(2H_2O)$ + H_2O, where these solutions are the base solutions in terms of weight–weight percentage (w/w %), and shows data of *p*H for PVA with changes of concentration with $CuCl_2(2H_2O)$ and their refraction index.

Concentrations of aqueous solutions			
Solution A + Solution B (w/w %)	Molecular weight (MW g/mol)	*p*H (a.u.)	Refraction index (a.u.)
10:1	20.024	3.4682	1.5005
10:1.5	21.687	2.8277	1.5085
10:2	23.349	2.4267	1.5155
10:2.5	25.012	2.3565	1.5176
10:3	26.674	2.1785	1.5181
10:5	33.324	1.7403	1.5200

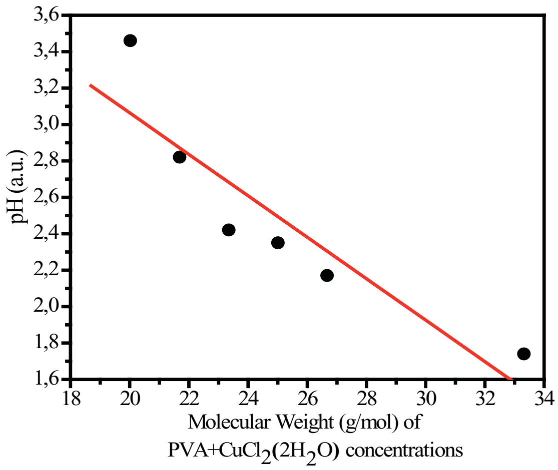


Fig. 1 The *p*H parameter indicates hydrogen potential in each aqueous solution for different molecular weights of PVA + $CuCl_2(2H_2O)$.

Table 1 we can see *p*H parameter values for different concentrations of photosensitive agent and Fig. 1 shows their *p*H behavior where the proportions of $CuCl_2(2H_2O)$ were changed.

By means of linear behavior of *p*H values, we can see that our photosensitive material has a chemical and physical stability. When we used a greater concentration of $CuCl_2(2H_2O)$ the *p*H was lower and the solution was acidic. Metallic ions mixed into H_2O molecules are in a complex form (they have been formed by aqua-ions). The formation of complex ions have a stability in an aqueous solution. It is given by their own aqua-ions, where H_2O molecules are joined by each ion for the direct bond of metal–oxygen. Metallic ions are enclosed by this molecules.[9] Complex ions stability from different solutions is very quick, and it implies an advantage since we would be able to manipulate solutions and it permits to accomplish samples for holographic register.

The sample preparation procedure is as follows: An appropriate volume of material is deposited on a glass substrate. Viscosity must be high enough to prevent free flow of material over the glass substrate. Optical characteristics of samples such as refraction index parameter are influenced for the different concentrations of $CuCl_2(2H_2O)$, as we can see in Table 1. The refractive indexes were measured with an Abbe refractometer (model Vista C10®); the values of this parameter are modified when samples have more density because metallic salt concentration is higher.

In particular, samples with 10:5 concentrations show crystallization due to high salt concentrations. This crystallization generates opacity and scattering in the surface sample, difficulty holographic register. When preparing the 10:5 concentrations, most of the time it crystallizes, however there are samples that do not crystallize and holographic gratings can be recorded, but they usually have a lower efficiency.

A necessary condition for holographic register is that samples have to be translucent; this characteristic facilitates gratings register and their reconstruction.

The different concentrations of a photosensitive agent, mainly in a thick film, determine its photosensitivity.[10] Thus, the absorbance profile of each sample to different

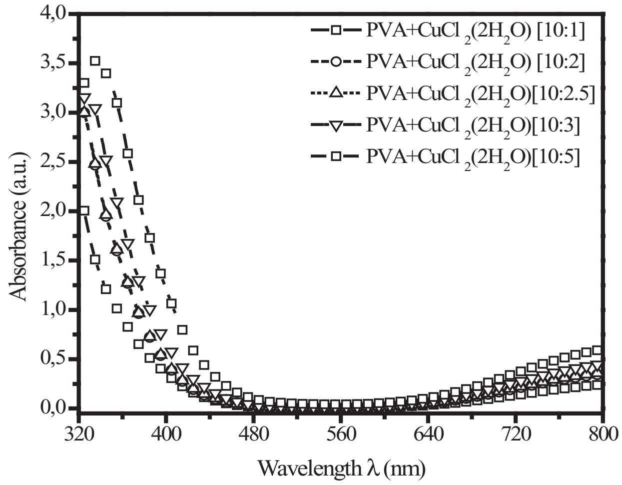


Fig. 2 Absorbance profile for different concentrations of PVA + $CuCl_2(2H_2O)$.

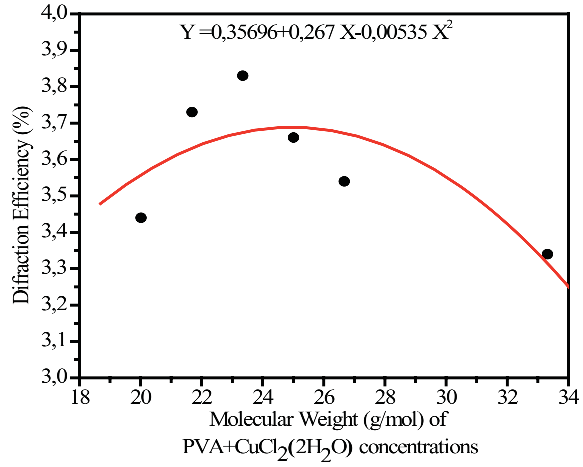


Fig. 4 Diffraction efficiency under Bragg condition regarding different molecular weights of PVA + $CuCl_2(2H_2O)$ concentrations.

concentrations of the photosensitive agent is affected, as shown in Fig. 2. The absorbance profile amplitude shows behavior of spectral response as a function of wavelength irradiation used. In this work we use five samples with different concentrations as described in Fig. 2.

The absorbance was measured with an UV-visible spectrometer (Perkin Elmer Lambda 3B®) with samples deposited on the glass substrate. Where samples have a small absorbance in the visible zone, it has high absorbance over the UV range; therefore it opens, the possibility to use samples with applications in this range.[11]

2.2 *Optical Setup*

This optical setup was used with symmetrical arms from Mirror 1 and Mirror 2 for holographic recording of diffraction gratings with material which was sensitized with $CuCl_2(2H_2O)$. In Fig. 3, we can see which are the optical components used to generate an interference zone. The source we use for holographic recording is a He–Cd laser at 442 nm (Ominichrome® Series 56), with an output power up to 5 mW. The beam incident on holographic material is linearly polarized; we ensure polarization using a linear polarizer since laser output after alignment on Mirror 3 and Mirror 4. For both arms A and B are linearly polarized, and also have a geometric symmetry forming an isosceles triangle between Mirror 1, Mirror 2, and the interference zone. The main beam is split into two arms using a cube beam splitter (CBS) prism; the angle formed between both arms is θ. The incident energy of both arms is not necessarily the same, but always tries to be 50% and 50%. The two beams impinge at a point (interference zone) where it forms an interference pattern.

This symmetry allows us to vary distance Z, between interference zone and point P, several positions in order to have various angles which in turn lead to multiple frequencies for holographic gratings which are necessary to obtain the module of transfer faction (MTF) parameter as will be shown in Fig. 8, where 15 measurements were made for this figure.

The size of the interference zone can be changed if we place a collimator before the prism system and worked with an interference area of approximately 5 mm in diameter; its size also varies depending on the angle between arms of array and interference zone, due to an astigmatic effect of producing flat reflective surfaces Mirror 1 and Mirror 2, respectively, and build a diffraction zone volume.[12]

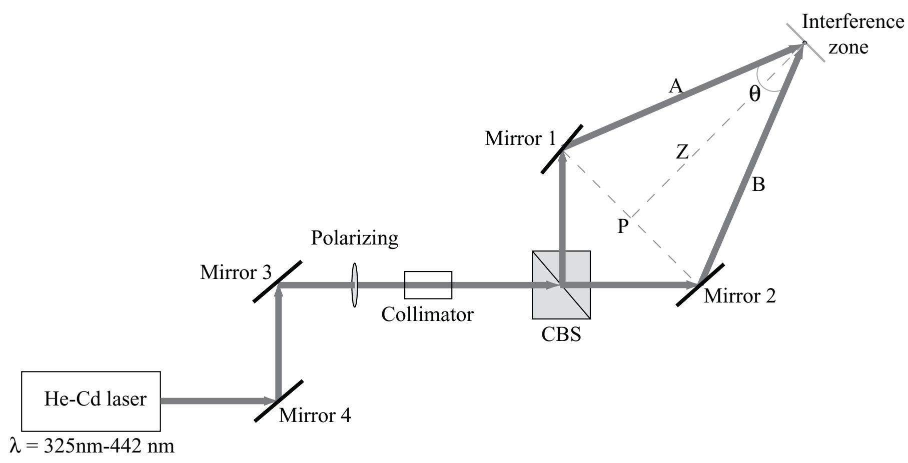


Fig. 3 Experimental setup for the recording of holographic gratings. Recording beam at $\lambda = 442$, where CBS: cube beam splitter.

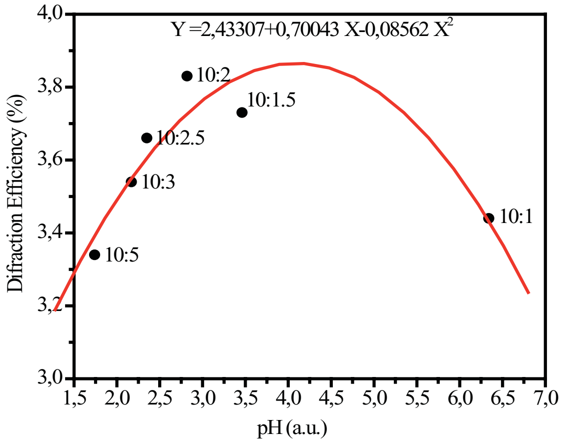


Fig. 5 Diffraction efficiency under Bragg condition regarding *p*H of PVA + $CuCl_2(2H_2O)$ concentrations.

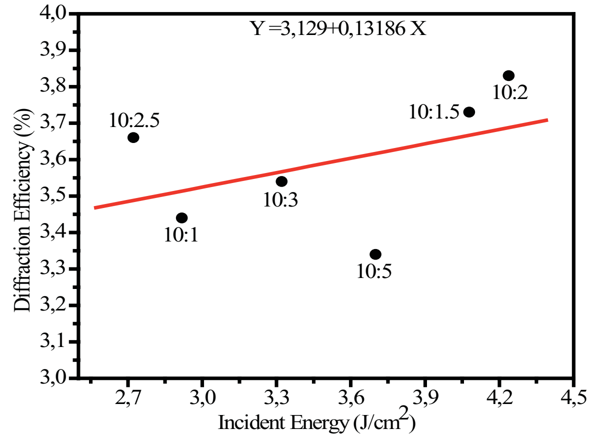


Fig. 7 Dependence of diffraction efficiency on exposure energy of each PVA + $CuCl_2(2H_2O)$ concentrations.

3 Experimental Results

The holographic gratings recorded in the photosensitive material were characterized with a continuous He–Ne laser at 632 nm (Melles Griot®), with output power of 10 mW. Thus we obtained the diffraction efficiency regarding physic-chemical characteristic of samples.

First, we obtained diffraction efficiency regarding a different concentration of $CuCl_2(2H_2O)$. Diffraction efficiency at Bragg condition was obtained. Figure 4 shows the results.

Under this condition, diffraction efficiency η will be studied and it can be expressed using Kogelnik's coupled[13] wave theory as:

$$\eta = \sin^2\left(\frac{\pi d \Delta n}{\lambda \cos\beta}\right), \tag{1}$$

where d is sample thickness, Δn is grating refractive index modulation, λ is wavelength, and β is readout angle inside photomaterial.

In this first experimental measurement and the next ones, diffraction efficiency is the intensity of a diffracted beam divided by the incident beam. This expression is common in holography and it does not take into account Fresnel losses by reflection and absorption.

3.1 *Diffraction Efficiency as a Function of Chemical and Physical Characteristic*

All experimental measurements of radiation were realized with a radiometer (Internacional Light, Modelo IL 1700®): to collect the total energy incident beam and transmitted of diffracted beam.

We have observed that, at low concentrations of salt $CuCl_2(2H_2O)$ in the PVA matrix is not present in photosensitivity, but when the concentration is very high, the photosensitivity occurs. Obviously, crystallization processes are observed if the relative humidity of the environment is above 35%. Controlling this parameter is possible when this salt makes a photosensitive emulsion. Due to high concentration of cupper chloride dihydrate $CuCl_2(2H_2O)$ in the PVA matrix, the material shows some degree of conductivity when the film is dry on the glass substrate and retains its elasticity. With the help of glycerol, it is observed that the crystallization process does not occur at a rate of 1 microliter per 10 milliliters of solution prepared. Preliminary results of this behavior are described in Sec. 3.4.

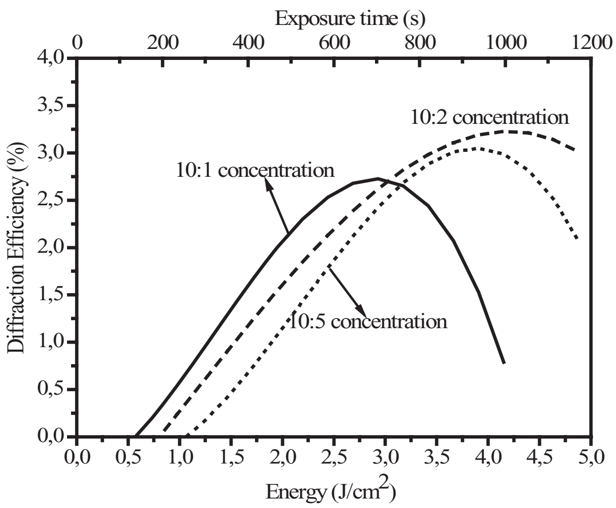


Fig. 6 Temporal evolution of diffraction efficiency during exposure time and energy for 10:1, 10:2, and 10:5 concentrations, respectively.

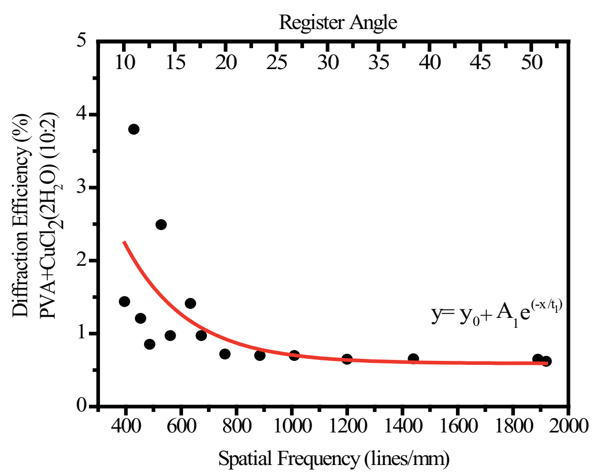


Fig. 8 Diffraction efficiency as a function of spatial frequency and register angle.

Figure 4 represents the diffraction efficiencies for each PVA + $CuCl_2(2H_2O)$ concentration denoted by the *x*-axis. Maximum diffraction efficiency was approximately 3.90%; it corresponds to 10:2 of concentration. A diffraction efficiency fit shows a nonlinear distribution regarding concentrations of $CuCl_2(2H_2O)$. This is represented by a polynomial fit: $Y = 0.356 + 0.267X - 0.0053X^2$; where Y corresponds to diffraction efficiency and X is ratio concentration in regard to molecular weight (MW), respectively. This equation describes the behavior of Fig. 4 of this pair of parameters.

There is a high relation between concentrations of photosensitive agents and *p*H of solutions as we can see in Fig. 1. Thus, maximum diffraction efficiency obtained for each concentration is affected by its *p*H, as we can see in Fig. 5. Represented by the polynomial fit: $Y = 2.433 + 0.7004X - 0.0856X^2$; where Y corresponds to diffraction efficiency, and X *p*H values, respectively. This equation describes the behavior of Fig. 5.

Both Figs. 4 and 5 show the maximum diffraction efficiency corresponding to ratio 10:2 concentration. These results indicate the chemical and physical stability of complex ions. The best results have been obtained with 10:2 concentrations; therefore these are optimum samples for a holographic register.

3.2 *Diffraction Efficiency as a Function of Exposure Energy*

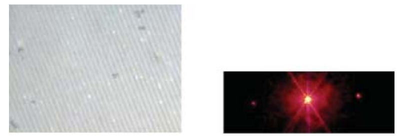
To confirm the chemical and physical stability of samples, we registered holographic gratings 24 h after. The exposure time was continuum in all samples, with a register intensity on holographic plane of $I_{\text{He–Cd}} = 4.8$ mW, such that the maximum diffraction efficiency is obtained. Figure 6 shows temporal evolution of grating efficiency under Bragg condition during holographic exposure. Concentrations 10:1, 10:2, and 10:5 are a good example of behavior of diffraction efficiency in register time and energy.

Finally, we obtained the incident energy necessary to obtain the maximum diffraction efficiency for each sample regarding their concentration as is shown in Fig. 7. Using the polynomial fit: $Y = 3.129 + 0.13186\,X$, where Y corresponds to diffraction efficiency, and X is incident energy (J/cm^2), respectively. This equation describes the behavior of Fig. 7. We can see the dependence of diffraction efficiency on exposure energy for each sample with different concentrations.

On the other hand, the samples with concentration of 10:5 (it represents 50% of the solution) had a process of crystallization. It was due to the concentration of $CuCl_2(2H_2O)$ producing a sample with a cracking appearance which the holographic register was not possible. This effect in film did not allow crosslinking should exist between polymer chains and it was not allowed in a holographic register in the material.[14]

3.3 *Diffraction Efficiency for Different Incident Angle*

We obtained dependence of diffraction efficiency regarding angle between the light of the writing beams. We plotted the angle (frequency) versus diffraction efficiency, see Fig. 8. It can be represented by a polynomial fit: $Y = Y_0 + A_1 \exp[-x/t_1]$, where Y corresponds to diffraction efficiency, and X is register angle (degrees), $Y_0 = 0.590$, $A_1 = 3.07532$, $t_1 = 5.8261$, respectively. With a register time of 10 min, the equivalent to 2.44 Joules/cm^2 of energy, for each one sample for a determinate angle. We obtained 15 holographic gratings, which represent 15 different values of incident angle; therefore 15 different samples with different frequencies; all samples were registered at the same exposure energy. From the Bragg equation it is possible to infer that to a bigger incident angle, decreased period, which is inverse of frequency, but diffraction efficiency value in this photosensitive material diminishes.



(a) (b)

Fig. 9 (a) Photograph of the gratings structure registered in the sample with 10:2 concentration. (b) Optical diffraction patterns of sample.

Figure 9(a) is a photograph of gratings structure registered sample with 10:2 concentration. Optical diffraction patterns of a sample with 10:2 concentration is shown in Fig. 9(b).

3.4 *Impedance Measurement of Photosensitive Material*

With a sample photosensitive to 10:2 it was observed that adding a small amount of glycerol, the effect of crystallization is reduced. The layer of photosensitive material retains its elasticity; this feature helps material showing a degree of conductivity was a measured impedance of material using a digital multimeter (Tektronix TX3®). When working with salt, $CuCl_2(2H_2O)$ mixed with PVA and glycerol is produced a material with a gel consistency. It has been observed that electricity is conducted better, using films with large thickness, and a greater concentration of salt. The impedance measurements were performed on a film thickness of 200 μm to environmental conditions. Figure 10 shows some results of impedance of this material combination, with a relative high ohmic value on the order of mega ohms (MΩ), showing that material has a modest range as a good electricity conductor as the metals. This material opens up the possibility to mix with other dopants and to reduce the impedance in photosensitive film.

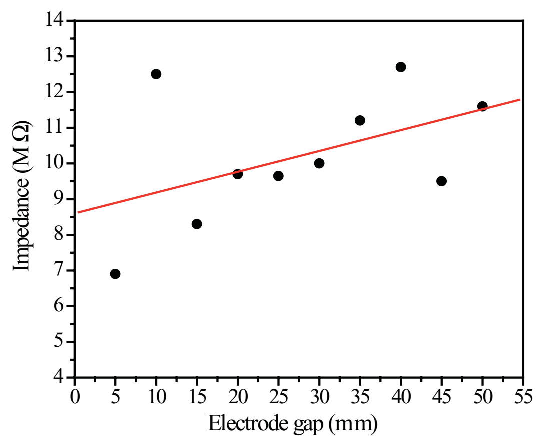


Fig. 10 Behavior impedance profile in regard to separation of electrodes on the surface of photosensitive film for 10:2 concentration.

There is a balance between reduced impedance and diffraction efficiency. It is noted that when adding a large amount of glycerol, we lose photosensitivity of material.

On the other hand it is not poured glycerol in sample, it hardens and is easy to crystallize, noting that the material is moderately sensitive, but not able to conduct electricity.

4 Conclusions

Results reported in this manuscript are still preliminary in regard to optimizing the diffraction efficiency capacity and spatial frequency modulation of material to work as a conventional holographic recording material. This opens the door for future research to optimize these parameters. However, experimental results exhibit an interesting feasibility of this material, which has a dual behavior. Photosensitivity and ability to conduct electricity showed modest results. It should be noted that making copper chloride dihydrate $CuCl_2(2H_2O)$ allowing both attributes to persist is an important achievement. Due to the nature of copper, there are generally photo-redox processes tightly surrounding the components, forming a strong crystallization. The fact that copper chloride dihydrate is allowed for easy assimilation into a matrix (PVA) is used to build our conductive and photosensitive film.

According to experimental developments there are relations between salts concentration and performance sample. When concentration is bigger than 50% of halide in a PVA matrix, the film darkens which sensibility increases. This was verified when we worked with minor concentrations to 10%, where it was not possible to obtain holographic gratings.

The samples concentration determines time and exposure energy to make a holographic recording. If concentration is minor, holographic recording needs major exposure time. The best result obtained was with a concentration ratio of 10:2, the exposure energy was of 4.23 Joules/cm^2, at a Bragg angle $\theta = 10.88$ deg.

To summarize, we obtained a holographic material with sufficient ability for holographic recording. It is a good candidate for holographic applications, it has stable behavior, is easy to use, and with low cost.

Holographic devices can be developed with this type of material with optimized parameters and can be prosecuted in areas such as micro-optoelectro mechanical system, and microelectromechanical system. It is a fact that a diffraction device dare to census information for small electric fields that makes this material attractive for technological implementation purposes.

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