

Article

Water Resistant Cellulose Acetate Based Photopolymer for Recording of Volume Phase Holograms

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Abstract: The development of environmentally robust photosensitive materials for holographic recording is crucial for applications such as outdoor LED light redirection, holographic displays and holographic sensors. Despite the progress in holographic recording materials development, their sensitivity to humidity remains a challenge and protection from the environment is required. One approach to solving this challenge is to select substrate such as cellulose acetate, which is water resistant. This work reports the development of a cellulose-based photopolymer with sensitivity of $3.5 \text{ cm}^2/\text{mJ}$ and refractive index modulation of 2.5×10^{-3} achieved in the transmission mode of recording. The suitability for holographic recording was demonstrated by recording gratings with the spatial frequency of 800 linepairs/mm. The intensity dependence of the diffraction efficiency of gratings recorded in 70 μm thick layers was studied and it was observed that the optimum recording intensity was $10 \text{ mW}/\text{cm}^2$. The robustness of the structures was studied after immersing the layer in water for one hour. It was observed that the diffraction efficiency and the surface characteristics measured before and after exposure to water remain unchanged. Finally, the surface hardness was characterized and was shown to be comparable to that of glass and significantly higher than the one of PVA-based acrylamide photopolymer.

Keywords: holographic recording materials; diffraction gratings; cellulose-based photopolymer



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1. Introduction

Holography is a method for the recording and retrieval of information, e.g., images or alphanumeric data, by utilizing interference and diffraction of light. As part of the holographic method, the interference pattern created by an object and a reference beam is recorded either in an analog form in a photosensitive medium or digitally, for example in an electrically controlled special light modulator. When the resulting analog or digital hologram is probed with the reference beam, they diffract light that carries information about the original object beam. The quality of the reconstructed object beam strongly depends on the quality of the hologram and in the case of the analog recording on the ability of the recording material to reproduce the varying intensity pattern/state of polarization pattern created by the coherent interfering beams. For that reason, research into the development of high quality holographic recording materials still attracts significant attention and effort among the academic- and industry-based research community. The targeted properties of the material are determined by the specific application, for example holographic optical elements for light redirection and shaping [1], archival data storage [2], security labels [3], metrology [4] and optical sensing platforms [5,6]. Nevertheless, some desirable properties are common for all applications—large dynamic range, high photosensitivity, mechanical

stability and robustness of the layers, low shrinkage during holographic recording and humidity/moisture resistance. The development of a novel holographic recording material is a complex process and relies on the careful choice of a number of chemical components and photochemical processes. Some of the most studied materials for holographic recording are emulsions utilizing silver halide chemistry [7], photopolymers [8], photoresists [9], photorefractive crystals and polymers [10], azo-dye polymers [11], photochromic materials [12] and photosensitive sol gels [13].

Silver-halide emulsions are highly sensitive, have very high resolution but they require a multistep wet chemical processing. Photoresist-based surface holograms require chemical processing and have a limited dynamic range. Photopolymers, due to their self-processing nature and the inherent flexibility of their design, in addition to the multi-component nature of the material, are particularly attractive for recording of volume phase holograms. Nevertheless, it must be kept in mind that the development of a low-cost and well-performing recording photopolymer material is a challenging task. The synthesis of new photopolymers aims at achieving materials with a large refractive index modulation and thus a large dynamic range, which are self-processing, have high photosensitivity, lack shrinkage due to photopolymerization and have high spatial resolution. In addition, temperature and moisture resistance ensure a long and stable post recording shelf-life of the hologram.

One approach for improving the environmental stability of the holographic recording layer is to introduce a matrix that is moisture and temperature resistant. This approach has been explored in the hybrid sol-gel technology which allows combining both organic and inorganic functional chemistries and provides a low temperature processing, usually at room temperature. Sol-gel materials for holographic recording prepared by combinations of functional oligomers or polymers with inorganic nanostructured compounds have been successfully reported [14]. This allowed the development of a new class of holographic recording materials that is more robust than conventional photopolymers and has a higher thermal and chemical stability, better dimensional stability and negligible shrinkage because of the rigid matrix [15,16]. The main challenge with the current sol-gel materials is related to the long gelation times, typically 5 to 21 days [16–23], required to achieve the solid phase of the material necessary for successful holographic recording.

Here we present another approach to obtaining a robust recording material by introducing cellulose as the matrix. Cellulose is biodegradable, sustainable, cheap, has excellent flexibility, is lightweight and environmentally friendly. It also has shown a great potential to replace conventional plastics [23]. This allows for fine-tuning of its properties as the porosity of cellulose layers can be modified by adding a pore former such as polyethylene glycol (PEG) [24]. PEG is hydrophilic in nature; it can be a colorless liquid or waxy solid and is soluble in water. Addition of more PEG increases the porosity of the membrane, but at the same time the layers can lose their robustness and can easily start wrinkling after exposure to water. Therefore, an optimum balance is needed in order to achieve control over the porosity while retaining resistance to water. The structure of PEG is commonly expressed as $H-(O-CH_2-CH_2)_n-OH$. Here in this research, the choice of CA-PEG is to replace the polyvinyl alcohol (PVA) binder which is used typically in acrylamide/PVA photopolymer materials [5]. The controlled porosity of the layers can be used to regulate the diffusion processes in them. Mass transport has been demonstrated to be taking place in photopolymers and to be critical for their performance [25]. Controlled porosity is also important in the development of holographic sensors where the rate with which the target analyte permeates the layer determines the response time of the sensor [26].

Several cellulose-based materials have been reported in the literature. Birabassov et al. fabricated azo-dye-doped cellulose films for holographic applications, where both intensity and the state of polarization of the light were recorded [27]. The results demonstrated that there are significant differences between the cellulose matrix and a polymer matrix such as polyvinyl alcohol (PVA) and PMMA, which are traditionally used for polarization holography in azo-dye polymers. [27]. Wang et al. presented a study of a new photosen-

sitive material comprising dichromated cellulose triacetate [28]. This matrix is a suitable medium of the dye molecules and has been used as a film to record gratings. The material is characterized by good environmental stability, strong surface relief modulation, light weight and flexibility [28].

Herein, we propose a novel holographic material based on cellulose acetate for recording of volume phase holograms. The proposed photopolymerizable mixture exhibits high refractive index modulation, along with low scattering and negligible shrinkage during photopolymerization. This photopolymer composition provides layers that remain stable after immersion in water and thus can be potentially used to develop sensors for detection of analytes in water solutions. The novel photopolymers consists of two acrylic monomers—acrylamide (AA) and N-N′methylenebisacrylamide (BA) and a photoinitiator, all dispersed within a polymer matrix known as binder. Holographic recording was carried out in a cellulose acetate (CA) and polyethylene glycol (PEG) based photopolymer containing N-phenyl glycine (NPG) as a photo initiator (Figure 1).

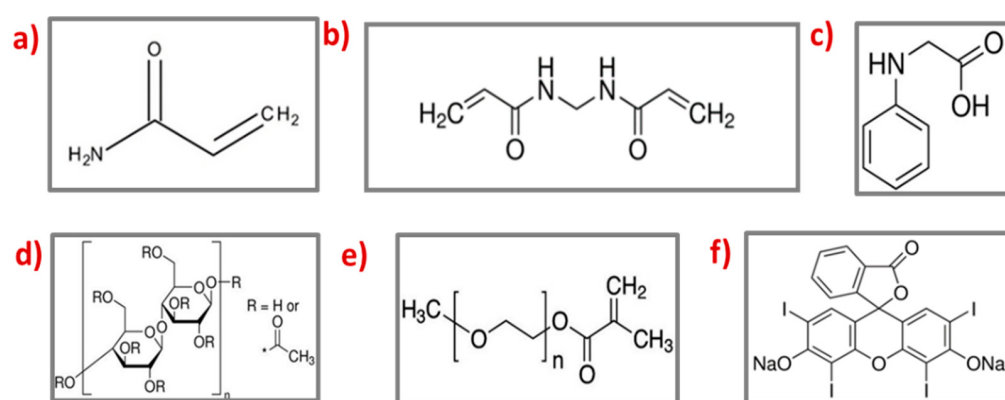


Figure 1. Chemical composition of the cellulose-based photopolymer: (a) acrylamide monomer; (b) N-N′methylenebisacrylamide—crosslinker; (c) NPG free radical initiator; (d) cellulose—binder; (e) polyethylene glycol—pore control agent; (f) erythrosine B—sensitizing dye and co-initiator.

The photoinitiator was selected because previous studies revealed that the diffraction efficiency of gratings recorded in photopolymer composition utilizing NPG as an initiator appeared to remain within 2% of the initial value when exposed to relative humidity changes in the RH range of 20–70% [29]. The use of the cellulose as a binder is appealing (Figure 2) because it is a non-toxic natural plastic, stable in water and has already been used to fabricate microfiltration membranes used to obtain safe drinking water [30]. Cellulose is an inexpensive and renewable biopolymer and readily available, which makes it a cheap raw material for various applications. CA matrix has good potential for fabricating sensors and biosensors [31] and because of that, the present research work aimed to develop a holographic sensor platform by using a CA–PEG blended composite photopolymer.

In the present article, to the best of our knowledge, a photosensitive layer composed of a CA–PEG blended composite for application in holography is reported for the first time. The recording ability of the photopolymer was investigated in a volume transmission mode of recording for a range of different recording parameters, including exposure energy and recording intensity. The refractive index modulation, the sensitivity, the robustness of the layers under exposure to water as well as their surface hardness have been characterized.

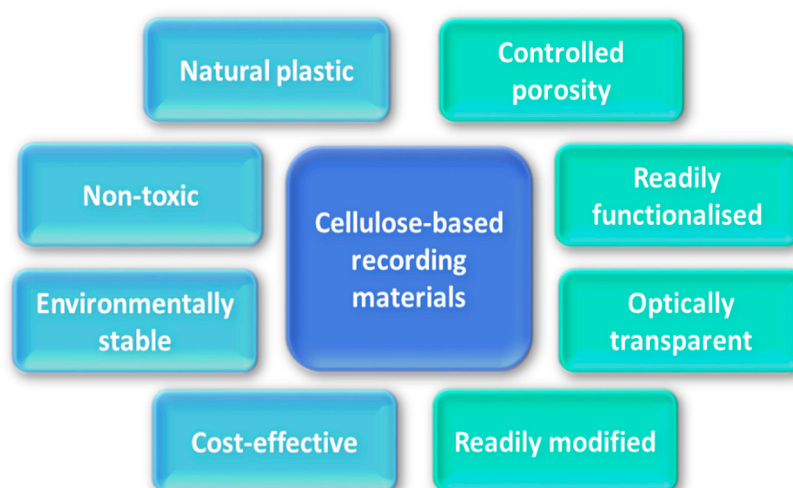


Figure 2. Key advantages of cellulose as a binder.

2. Theoretical Background

2.1. Evaluation of the Holographic Recording Material Properties

The properties of the holographic recording material are tested by recording the simplest hologram created by the interference of two plane waves—a holographic grating. By measuring the diffraction efficiency of the grating in real time it is possible to estimate the sensitivity of the material, as well as the photoinduced refractive index modulation and its stability over time. Depending on the recording geometry, spatial frequency of the interference fringes created by the two recording beams, probe wavelength and the physical characteristics of the recording layers, such as thickness or photoinduced refractive index modulation, there are two distinguished regimes of operation of the holographic grating—as a plane hologram or as a volume hologram. The diffraction efficiency of plane sinusoidal holographic gratings is limited to about 33%, they produce multiple orders and the diffraction pattern is produced at almost every angle of incidence of the probe beam. In contrast, the volume holographic gratings have one diffraction order, theoretically their diffraction efficiency can reach 100% and it strongly depends on the incidence angle of the probe beam. Two quantitative parameters have been introduced to predict in which regime the recorded grating will operate [32]. The material that has been studied in this article does not have extremely high refractive index modulation (for example as the 0.5 in DCG materials) and that is why it can be evaluated with the help of the Q parameter, Equation (1), introduced in [32].

$$Q = \frac{2\pi\lambda_0 d}{n_0 \Lambda^2} \quad (1)$$

where λ_0 is wavelength of the probe beam in vacuum, d is the thickness of the photosensitive medium, n_0 is the average refractive index of the recording material and Λ is the grating period.

The Q factor corresponding to the holographic gratings studied in this paper was calculated by using Equation (1) [32]. Unslanted volume transmission gratings with a spatial frequency of 800 linepairs/mm (period 1.25 μm) were recorded in the photosensitive layers with thickness of $70 \pm 3 \mu\text{m}$. According to Equation (1), these parameters correspond to a Q factor of about 119 and, thus, Kogelnik's Coupled Wave Theory [33] for the calculation of the diffraction efficiency/refractive index modulation can be applied. Moreover, the gratings are created as a spatial variation of the refractive index of the material caused by photopolymerization and spatially varying density. They change the phase of the propagating probe beam and are commonly named phase gratings. In this study, transmission volume phase gratings have been used to evaluate the holographic recording properties of the material.

2.1.1. Diffraction Efficiency of Volume Phase Gratings

The diffraction efficiency η of volume phase transmission holographic gratings is described with high accuracy by the Kogelnik's coupled wave theory [33], Equation (2).

$$\eta = \sin^2 \left(\frac{\pi \Delta n d}{\lambda p \cos \theta_B} \right) \quad (2)$$

where Δn is the refractive index modulation (the maximum difference between exposed and unexposed areas), λp is the wavelength of the probe beam inside the medium, θ_B is the Bragg angle inside the photosensitive material and d is the thickness of the grating. The real time recording of the diffraction efficiency provides valuable information about the photoinduced refractive index modulation, assuming that there is no accompanying change in the thickness of the layer due to shrinkage. The refractive index modulation was calculated from the diffraction efficiency by utilizing Equation (3) below.

$$\Delta n = \frac{\lambda p \cos \theta_B \sin^{-1}(\sqrt{\eta})}{\pi d} \quad (3)$$

where the meaning of the symbols is the same as in Equation (2).

2.1.2. Bragg Selectivity Curve

The sensitivity of the diffraction efficiency to detuning from Bragg angle is characterized by measuring the Bragg angular selectivity curve. By fitting the Bragg selectivity curve it is possible to estimate the thickness of the recorded volume grating structure. The Bragg selectivity curve is given by Equation (4):

$$\eta = \sin^2 \left(\frac{\Phi^2 + \chi^2}{1 + \frac{\chi^2}{\Phi^2}} \right)^{1/2} \quad (4)$$

where $\Phi = \frac{\pi \Delta n d}{\lambda p \cos \theta_B}$, is the phase difference between the transmitted (zero order) and the diffracted beam, $\chi = K \frac{\Delta \theta_B d}{2}$, is the phase detuning caused by deviation from Bragg angle $\Delta \theta_B$ and K is the grating vector magnitude.

2.1.3. Sensitivity of the Recording Material

The sensitivity of the recording material is an important parameter as it allows photo-sensitive layers prepared of materials with different chemical compositions be compared. It was determined with the help of the real time diffraction efficiency curve. The sensitivity S is related to the measured diffraction efficiency and the exposure energy delivered E through Equation (5):

$$\sqrt{\eta} = S.V.E/2 \quad (5)$$

where the V is the visibility of the interference fringes and is determined by the intensities of the two recording beams I_1 and I_2 and given by Equation (6):

$$V = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \quad (6)$$

3. Material and Methods

3.1. Materials

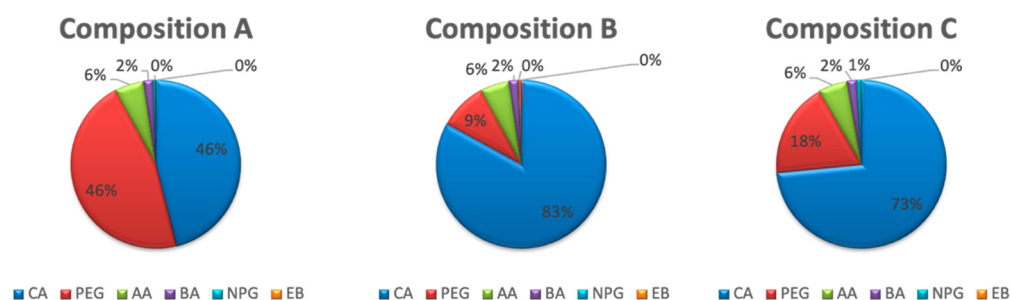
3.1.1. Photopolymer Composition

A number of cellulose-based photopolymer compositions were prepared as described in Table 1. Cellulose acetate (Mw 30,000 and acetyl content 39.8%), polyethylene glycol (Mw 950–1050) were dissolved in acetone. All the materials used in this research work were of analytical grade purchased from Sigma Aldrich without further purification.

Table 1. The amount of components added in the photopolymer solution (prepared in acetone 100 mL).

Components	(A) Amount (g)	(B) Amount (g)	(C) Amount (g)
Cellulose acetate (CA) (g)	5.0	9.0	8.0
Polyethylene glycol (PEG) (g)	5.0	1.0	2.0
Acrylamide (AA) (g)	0.6	0.6	0.6
N,N'-methylenebisacrylamide (BA) (g)	0.2	0.2	0.2
N-phenyl glycine (NPG) (g)	0.05	0.05	0.09
Erthrosine B dye (EB) (g)	0.0044	0.0044	0.0044
Total weight	10.854	10.854	10.894

Table 1 shows the chemical composition of photopolymers A, B and C in order to develop a new formulation for the fabrication of a volume hologram. In order to facilitate the comparison of the photopolymers used in this study, pie charts of the four compositions are shown in Figure 3. For all compositions the amount of CA-PEG was varied to obtain good optical quality layers which are less sensitive to water and able to record high diffraction efficiency gratings. After optimization composition C was used further studies. The amount of initiator was optimized in order to achieve better sensitivity and higher diffraction efficiency.

**Figure 3.** Chemical composition of the dry photopolymer layers (% *w/w*).

3.1.2. Photopolymer Solution Preparation and Layer Coating

In order to obtain CA-PEG blended solution stock solution of 8% *w/w*, cellulose acetate (CA) was dissolved in 100 mL of acetone with constant stirring at 80 °C for 3 h in a fume hood. To obtain a homogenous CA-PEG solution, the corresponding amount of PEG was added with regular stirring at 80 °C for another 3 h. A viscous and clear solution was obtained which was termed as a blended solution, CA-PEG (Figure 4).

**Figure 4.** Cellulose acetate and polyethylene (CA/PEG) blended solution.

The solution was allowed to cool down to room temperature (20 °C) for approximately 4 h. Next acrylamide (AA) and N,N'-methylenebisacrylamide (BA) were added as the two monomers. Then N-phenyl glycine (NPG) initiator [34] was added into the CA-PEG solution. Erythrosine B (EB) was directly added as dye powder into the solution at the end. Finally, all the components were mixed for 2 h at room temperature. Then, 700 μ L volume of the photopolymer solution was spread evenly on a glass substrate.

A CA and PEG blended solution was prepared in acetone as a solvent. The layers of CA-PEG were initially coated on a microscope glass slide. The quality of CA-PEG layer was not very good in the first instance, as acetone is a very volatile solvent, and it was observed that such thin layers dry very quickly. In order to improve the layer quality, the layers were covered with a glass petri dish as shown in Figure 5a, and the rate of evaporation of the solvent decreased and a better quality of layer was obtained; Figure 5b shows the high optical quality of layers after drying. The flow-chart of the chemical procedure involved in the layer preparation is shown in Figure 5c.

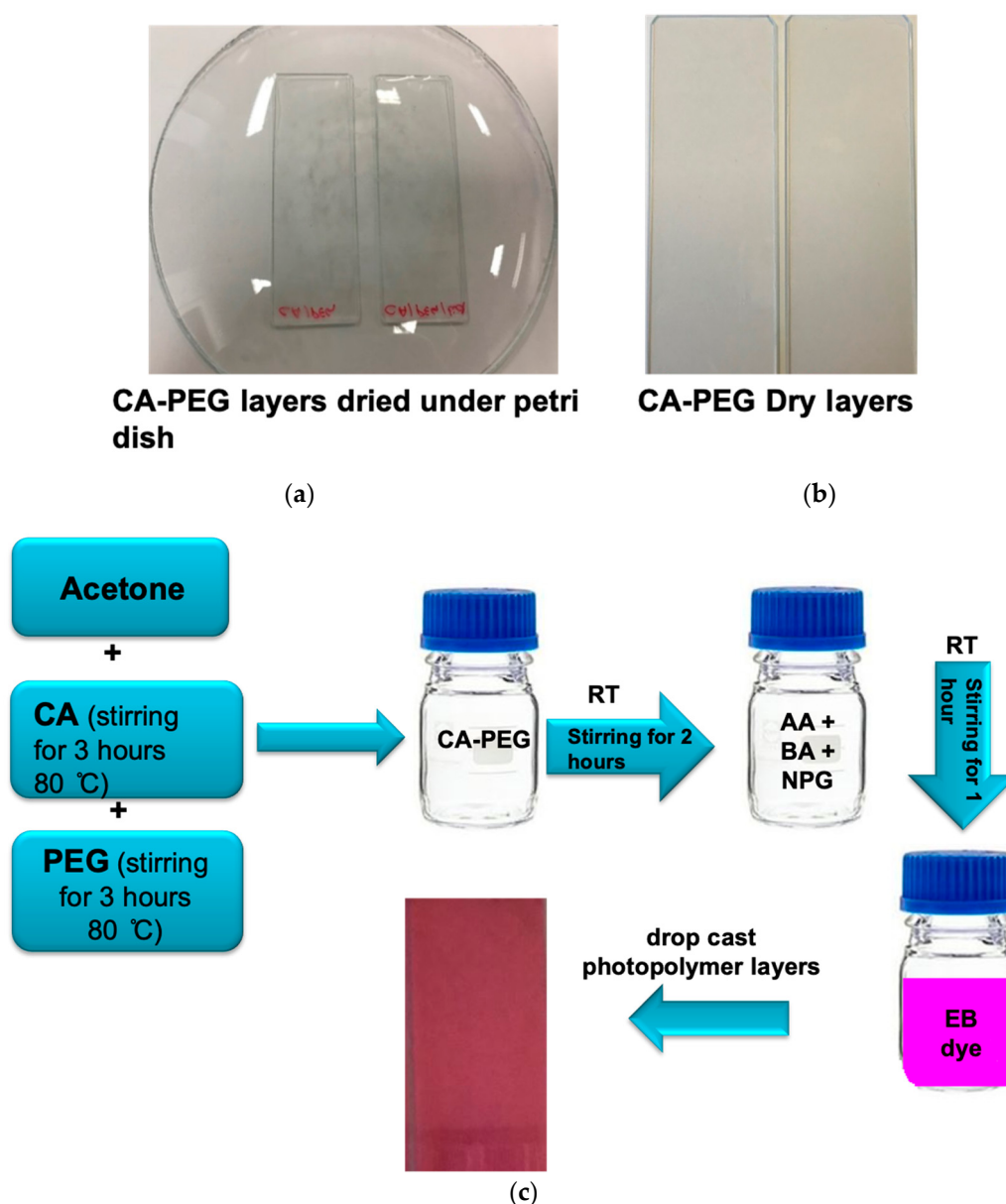


Figure 5. Pictures of (a) layers drying under a petri dish and (b) dried layers; (c) flow chart of photosensitized sample preparation.

3.2. Recording and Testing of the Holograms

The holographic setup for recording transmission volume phase gratings is shown in Figure 6. The recording was carried out on an optical table (Newport RS 4000), which was floated in order to minimize vibrations. The photopolymer layers were exposed to two coherent beams of Nd:YVO4 laser operating at a wavelength of 532 nm. The incident angles of the two beams were identical and thus the recorded grating was unslanted. The incident angles of the recording beams in air were 12.3° and this resulted in the recording of a diffraction grating with a spatial frequency of 800 linepairs/mm. A low intensity (2.5 mW/cm^2) Helium–Neon (He–Ne) laser beam operating at a wavelength of 632.8 nm was utilized as a readout beam to monitor the buildup dynamics of the grating, as the photoinitiator in the present system is insensitive at this wavelength. The intensity of the diffracted beam was measured by an optical power meter (Newport 1830-C), and the acquired data were transferred to a computer in real time with the help of a LabView program. The diffraction efficiency η of the transmission gratings was calculated as the ratio of the intensity of the 1st order diffracted beam and the intensity of the incident beam.

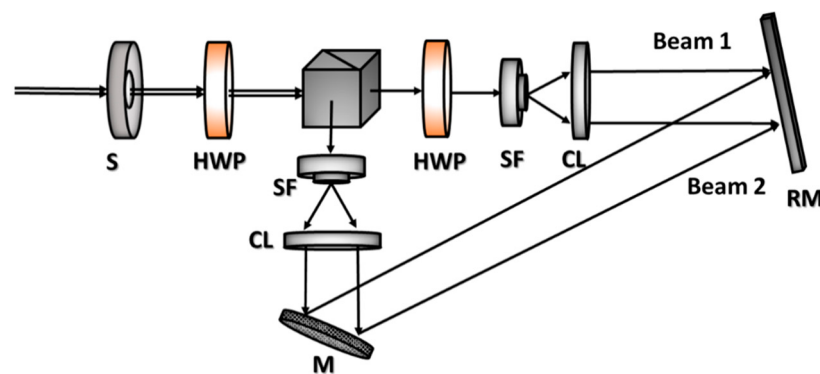


Figure 6. Experimental set up for recording transmission gratings (S—shutter; HWP—half wave plate; PBS—polarizing beam splitter; SF—spatial filter; CL—collimator; M—mirror; RM—recording material).

3.3. Data Analysis

The thickness of the layers was estimated from the measured post recording Bragg selectivity curve which was fitted to Kogelnik's formula (4) for an unslanted transmission holographic grating [33].

The refractive index modulation was determined from the maximum diffraction efficiency with the help of Equation (3).

As the intensity of the two recording beams was carefully adjusted to be the same, the visibility of the fringes V was assumed to be 1. The sensitivity was estimated after fitting the linear part of the $\sqrt{\eta}$ (E) for each recording intensity.

3.4. Characterisation of Materials Hardness

A pendulum hardness apparatus was used for the coating hardness evaluation. The test consists of measuring the damping time of a pendulum oscillating on a test surface. The hardness is a function of the oscillation amplitude, detected by electronic optical cells from two specified pendulum deflection positions. The lower the value of oscillations indicated the softer the material.

4. Results

4.1. Preliminary Screening of Layers of Different Thickness

Initial studies to test for the optimum thickness of the layers and recording intensity were carried out by recording transmission holographic gratings of spatial frequency of 800 linepairs/mm for 30 s. The exposure time was selected with the view of real time applications. Previous experience with photosensitive materials for real time applications [4]

reveal that 30 s exposure time can allow for a reasonable rate of production and cost of the photonic devices. The samples were recorded for a constant exposure time of 30 s with intensity varying from 3 to 15 mW/cm². At this stage only the final diffraction efficiency was measured. As seen from Figure 7a, the recording in the 70 µm thick layer consistently achieved higher diffraction efficiency at lower exposure energies.

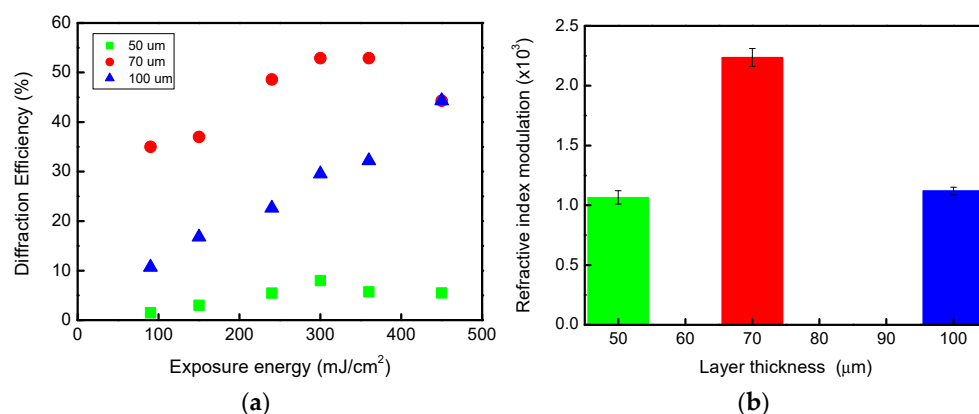


Figure 7. (a) Measured diffraction efficiency vs. exposure energy for the volume transmission gratings recorded in composition C with varying recording intensities 3–10 mW/cm² at fixed time 30 s and spatial frequency of 800 l/mm was investigated for sample thickness of 50, 70 and 100 µm (± 5 µm) layers, (b) Δn vs. layer thickness 50–100 µm ± 5 µm for CA-PEG photopolymer composition.

It can be seen that the recorded DE in the thicker layers has not achieved saturation at 450 mJ/cm². Shorter recording times and lower recording intensity was targeted in terms of developing a material for practical applications. Comparison of the refractive index modulation in the three sets of samples is shown in Figure 7b. It is evident that the maximum achieved refractive index modulation in the studied range of intensities is observed in layers of 70 µm and for that reason, we have proceeded with this layer thickness. All further experiments were performed in triplicate by repeating the recording in three separate layers. The typical real time diffraction efficiency curve, calculated real time refractive index modulation and Bragg selectivity curve measured after the recording are shown in Figure 8.

4.2. Intensity Dependence of the Holographic Recording

The intensity dependence of the recording process in 70 µm thick layers was studied in more detail in the range of 3–15 mW/cm², by recording real time diffraction efficiency curves and Bragg selectivity curves immediately after recording. The results are shown in Figure 9. The maximum exposure energy was kept constant at 300 mJ/cm², and to achieve that the total exposure time for each intensity was adjusted accordingly. The real time diffraction efficiency data (Figure 9a) and the diffraction efficiency dependence on total exposure (Figure 9b) reveal that recording with an intensity of 10 mW/cm² achieved the fastest recording and the highest diffraction efficiency. The Bragg selectivity curves in Figure 9c show different order of the maximum diffraction efficiency and the reason for that is that they have been measured at the end of the holographic recording. The Bragg curves have the typical volume diffraction gratings shape and imply a uniform distribution of the refractive index modulation throughout the layer. The maximum achieved refractive index modulation, Figure 9d was determined from the peak diffraction efficiency and was 2.5×10^{-3} , which is comparable to the refractive index modulation observed in acrylamide photopolymers in PVA matrix [35].

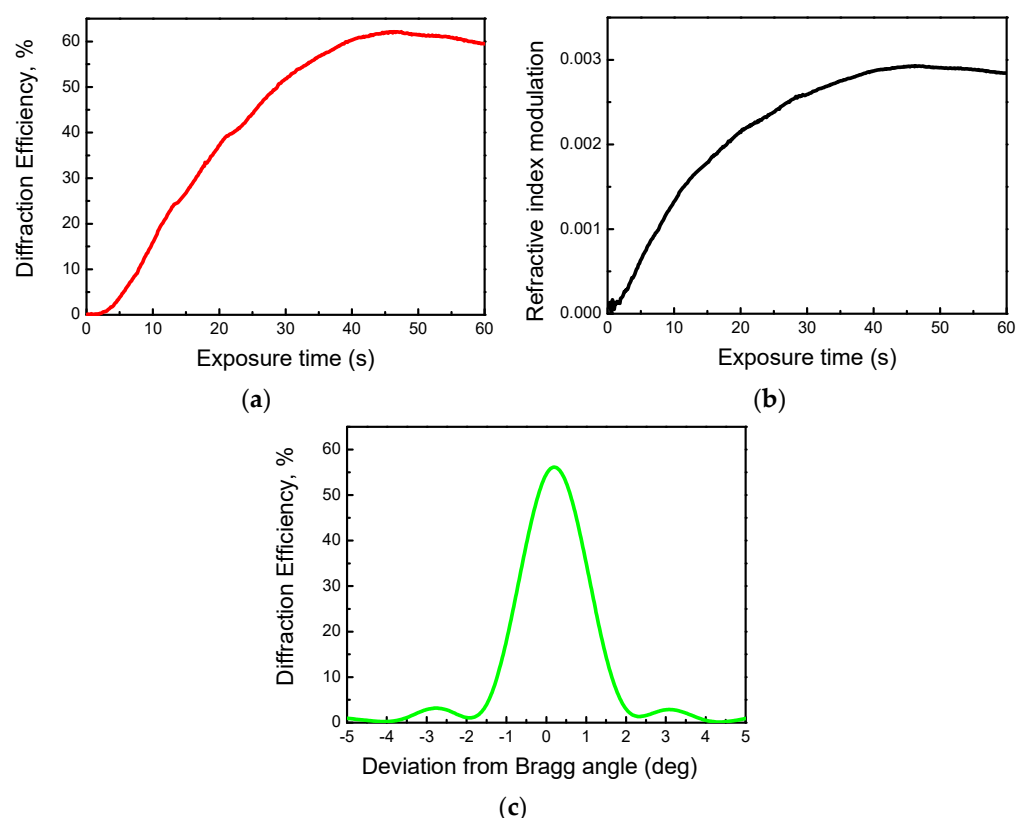


Figure 8. Example curves obtained during and after recording in layers of 70 μm thickness prepared from composition C. (a) Real time diffraction efficiency; (b) refractive index modulation; (c) Bragg selectivity curve.

4.3. Durability of the Recorded Grating in Water

In order to verify that the introduction of a cellulose binder leads to a stable diffraction grating that can be used in water and in high humidity environment, the grating was immersed in water. The temperature of the water was 21 degrees (room temperature). The diffraction efficiency was measured every 5 min for up to an hour, Figure 11a. The duration of the experiment was determined based on previous studies of holographic sensors for operation in water based solutions [5,26] where the response of the sensor to the target analyte was within less than 5 min. For other target applications, a different/longer duration of the exposure to water may be necessary. The Bragg selectivity curve before and after exposure to water Figure 11b.

4.4. Sensitivity of the Layers

In order to calculate the sensitivity of the layers the $\sqrt{\eta}$ was plotted versus recording exposure energy, Figure 10a and the linear part of the curve was fitted to obtain the sensitivity S according to Equation 5. As seen from Figure 10b the sensitivity peaks for recording intensity 10 mW/cm^2 at 3.5 cm^2/mJ . Again this sensitivity is similar to the sensitivity in acrylamide/PVA based photopolymer, which implies that the diffusion and polymerization processes governing the holographic recording are not dramatically influenced by the change of the binder matrix. The added benefit of the cellulose binder is coming from the durability of the layers when exposed to water and this is studied in more detail in the following section.

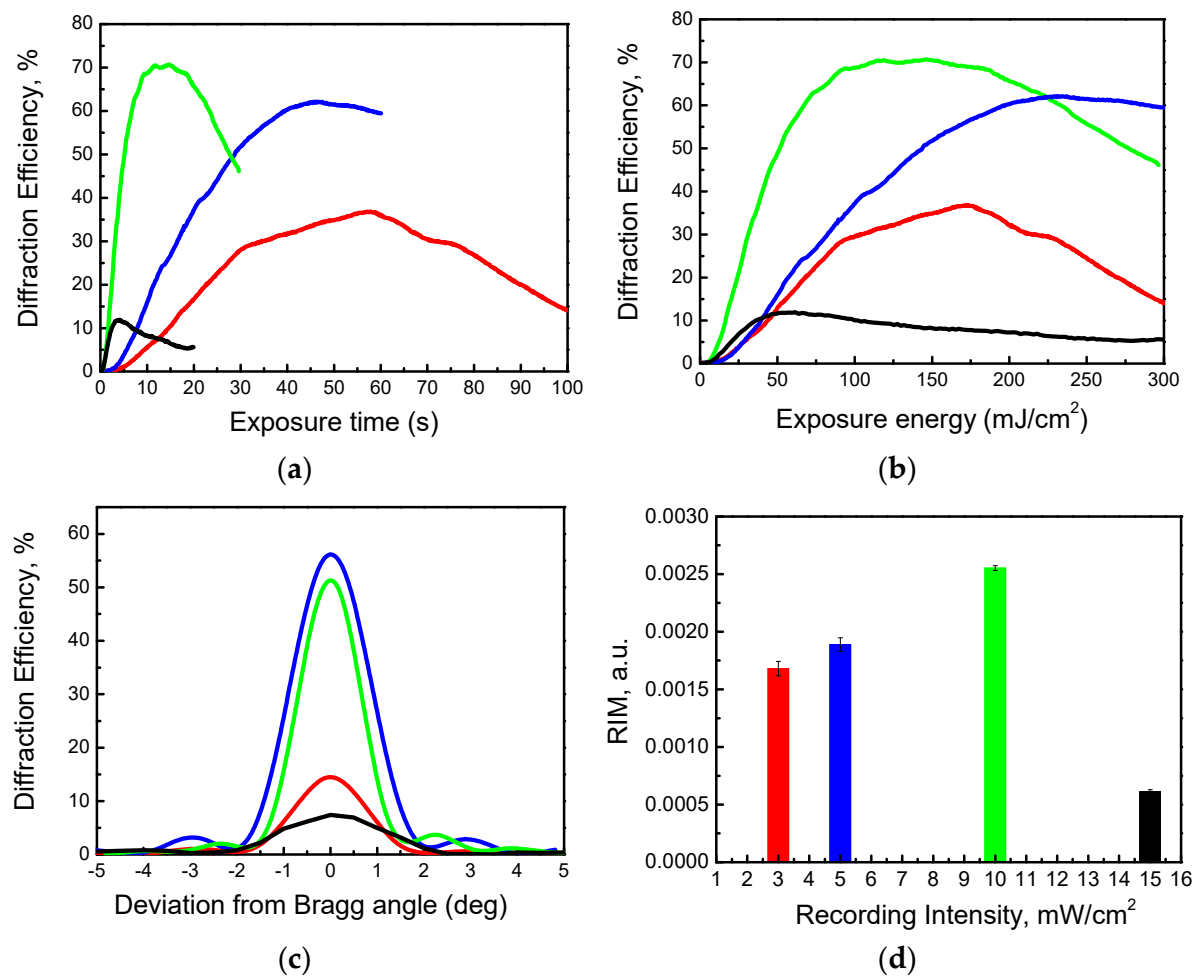


Figure 9. Recording of grating with spatial frequency of 800 linepairs/mm with total intensity of 3 mW/cm² (red), 5 mW/cm² (blue), 10 mW/cm² (green) and 15 mW/cm² (black). (a) Diffraction efficiency of the grating versus exposure time; (b) diffraction efficiency versus exposure energy; (c) Bragg selectivity curves for the gratings; (d) maximum achieved refractive index modulation. Experiments are performed in triplicate.

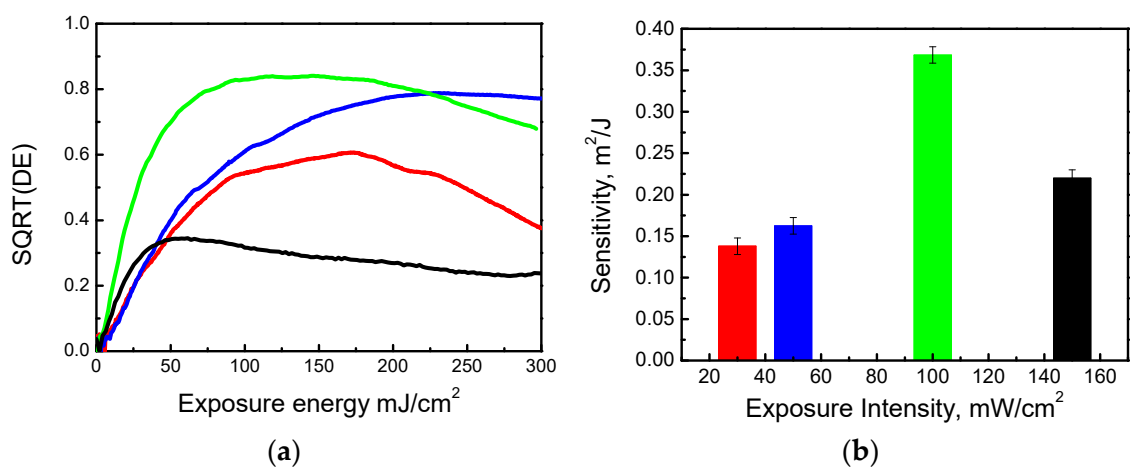


Figure 10. Characterization of the sensitivity of the layers of 70 μm thickness for recording at 800 linepairs/mm at different recording intensities: (a) $\sqrt{\eta}$ versus exposure energy; (b) sensitivity depending on the recording intensity.

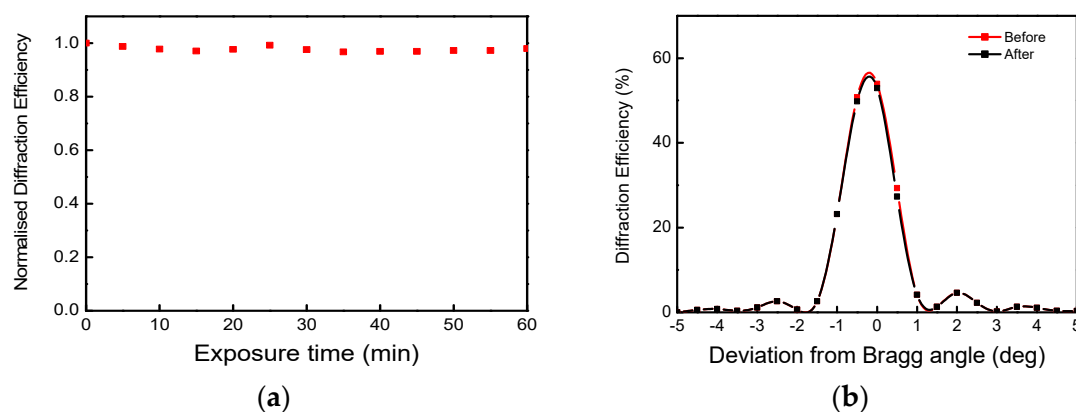


Figure 11. (a) Normalized diffraction efficiency of a grating recorded in $70 \pm 5 \mu\text{m}$ thick layer, spatial frequency of 800 linepairs/mm, recording intensity $5\text{mW}/\text{cm}^2$ and total exposure energy $300 \text{ mJ}/\text{cm}^2$; (b) Bragg selectivity curves before (black) and after exposure (red) to water for 60 min.

The surface of the layers was characterized by AFM before Figure 12a and after exposure to water Figure 12b and it was observed that no significant deterioration takes place in the water.

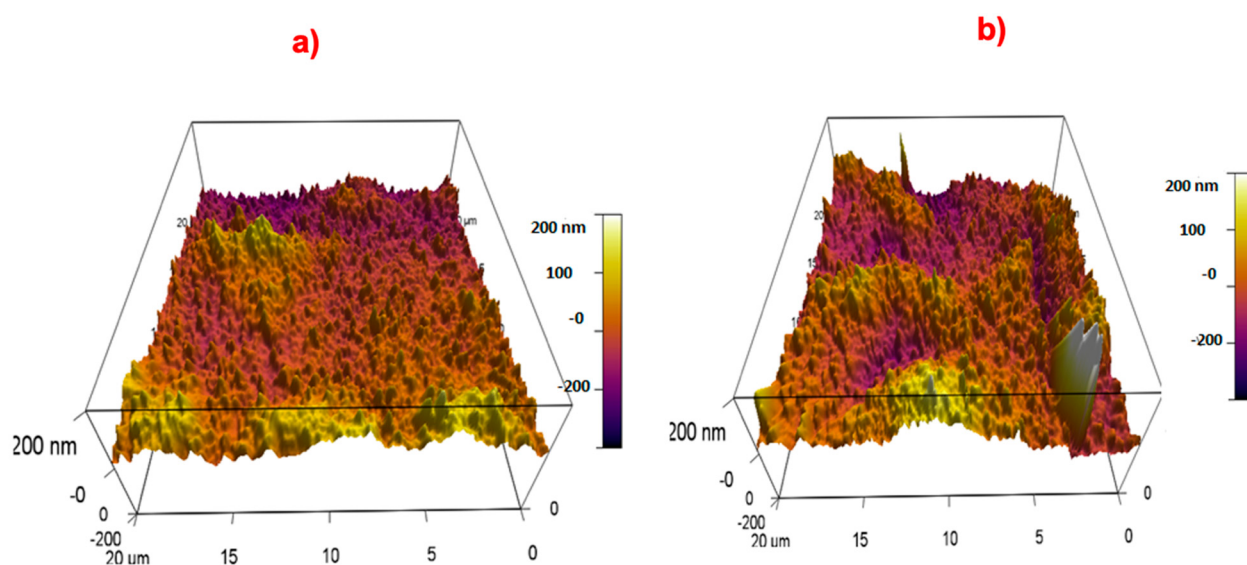


Figure 12. AFM images 3-dimensional view of: (a) CA-PEG recorded volume hologram; (b) CA-PEG recorded volume hologram exposed to water (spatial frequency 800 linepairs/mm).

4.5. Characterisation of the Hardness of the Layer Surface

Finally, the robustness of the layers was evaluated by a pendulum test where the number of oscillations with an amplitude above a threshold value were measured for pure glass, pure cellulose, photosensitive cellulose layer and an acrylamide/PVA based photopolymer. The higher the number of oscillations the higher the hardness of the layer. The results in Figure 13 reveal that introducing cellulose as a matrix has a dramatic improvement on the hardness of the layer and makes it comparable to pure glass. This is a very significant effect, because typically the harder layers of the monomer have a much slower diffusion rate, and it is very difficult to achieve the same sensitivity in a holographic recording. Due to the porous nature of the cellulose, binder improvement in the hardness of the layer was possible without decrease in the achieved refractive index modulation and sensitivity.

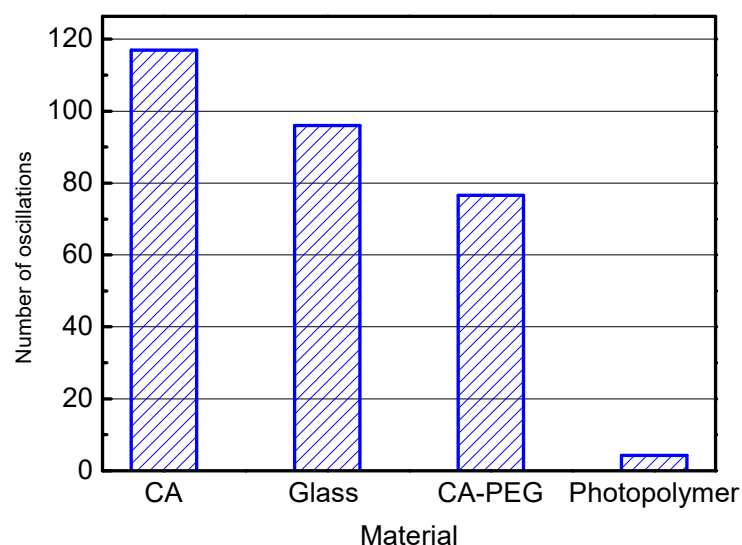


Figure 13. Pendulum hardness studies of CA, glass substrate, CA-PEG and photopolymer.

5. Discussion

In holographic sensors research, the interest in biopolymers, environmentally friendly polymers and photopolymers containing PEG has been increasing in recent years in relation with their use in liquid environments [36,37]. Most of the materials that are developed are used for the recording of reflection holograms because they can be used as visual indicators of the presence and concentration of the target analyte. For example, a water resistant photopolymer for holographic recording utilizing PEG has been previously used for recording reflection gratings for detection of glucose [37]. To demonstrate the concept a poly(acrylamide-co-poly(ethylene glycol) diacrylate) hydrogel backbone was functionalized with 3-(acrylamido)phenylboronic acid to produce a reversible response to variation in glucose concentration, which was correlated with Bragg peak shifts to obtain quantitative measurements. The diffraction efficiency of the Bragg stack recorded in a 10 micrometer hydrogel layer was measured to be 9%, which implies refractive index modulation in the order of 5×10^{-3} . Although this value is of the same order as the one produced in the composition described in the present article— 2.5×10^{-3} (Figure 9d), it should be kept in mind that there is a significant difference in the spatial frequencies of the gratings presented here and those in [37].

Another study [28] reports holographic recording in dichromated cellulose triacetate ~DCCTA with maximum diffraction efficiency of 60% achieved in transmission mode of recording of gratings of spatial 20 linepairs/mm. The gratings require post-recording chemical processing and depending on the spatial frequency a surface relief profile of 0.5 to 6 μm is observed. In the material reported in this study no surface relief modulation is observed as clearly seen in Figure 12.

The increased stability of the recorded holograms (Figures 11 and 12) is mainly attributed to the use of cellulose acetate as a binder. This is supported by previous studies [27] where cellulose acetate based material has been used for recording of polarization holograms. It has been observed that the use of CA plays a significant role in the orientation mobility of the anisotropic dye and the achievement of photoinduced effects with higher stability.

A widely studied environmentally friendly photopolymer is based on acrylamide as a monomer and a polyvinyl alcohol (PVA) as a binder [5]. This material is initially water-soluble and after photopolymerization a non-toxic hydrogel is produced. The response of holographic gratings to humidity and temperature recorded in different derivatives of this material is well-documented [5,6,29]. While it is well suited for the development of humidity and temperature sensors, its sensitivity to these external factors is highly unde-

sirable when other analytes are targeted. It is worth mentioning that the cellulose based material presented in this study has similar sensitivity and refractive index modulation while the diffraction efficiency of the recorded gratings is practically independent on the presence of water in its environment, which makes it an excellent candidate for use in holographic sensing.

6. Conclusions

A new photopolymer formulation based on CA–PEG blend was developed; volume holograms were recorded successfully with this formulation. The recording conditions and thickness were optimized at 800 linepairs/mm. The novel formulation was found to be stable in water environment. A maximum η 70% was measured in growth curves, and maximum refractive index modulation of $\Delta n = 2.6 \times 10^{-3}$ was estimated. Moreover, the CA–PEG polymers used in this study contain a biopolymer, which is promising and leads to sustainable chemistry. The response to DI water was also investigated and the results are very promising as the diffraction efficiency does not drop down after exposure to water for 60 min. Intensity dependence characterization studies show that the material has a good response to a large range of intensities. It allows for exposure times to be significantly reduced via the use of higher recording intensities, which is a desirable feature for industry applications that would reduce production times. AFM measurements provided information at the surface level. One of the key advantages of cellulose-based holograms is that they can easily be peeled off and thus they can be used in the applications where self-standing holograms are needed. The recorded holograms were found to be stable, robust and reproducible.

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References

1. Naydenova, I.; Akbari, H.; Dalton, C.; Mohamed Ilyas, M.Y.; Tee Wei, C.P.; Toal, V.; Marti, S. Photopolymer Holographic Optical Elements for Application in Solar Energy Concentrators. In *Holography—Basic Principles and Contemporary Applications*; Mihaylova, E., Ed.; InTech: London, UK, 2013.
2. Ashley, J.; Bernal, M.-P.; Burr, G.W.; Coufal, H.; Guenther, H.; Hoffnagle, J.A.; Jefferson, C.M.; Marcus, B.; Macfarlane, R.M.; Shelby, R.M.; et al. Holographic data storage technology. *IBM J. Res. Dev.* **2000**, *44*, 341–368. [\[CrossRef\]](#)
3. Vather, D.; Naydenova, I.; Cody, D.; Zawadzka, M.; Martin, S.; Mihaylova, E.; Curran, S.; Duffy, P.; Portillo, J.; Connell, D.; et al. Serialized holography for brand protection and authentication. *Appl. Opt.* **2018**, *57*, E131–E137. [\[CrossRef\]](#)
4. Shakher, C.; Rao, G.V. Use of holographic optical elements in speckle metrology: Part 2. *Appl. Opt.* **1987**, *26*, 654–657. [\[CrossRef\]](#)
5. Cody, D.; Gul, S.-E.; Mikulchyk, T.; Irfan, M.; Kharchenko, A.; Goldyn, K.; Martin, S.; Mintova, S.; Cassidy, J.; Naydenova, I. Self-processing photopolymer materials for versatile design and fabrication of holographic sensors and interactive holograms. *Appl. Opt.* **2018**, *57*, E173–E183. [\[CrossRef\]](#)
6. Yetisen, A.K.; Naydenova, I.; Vasconcellos, F.D.C.; Blyth, J.; Lowe, C.R. Holographic Sensors: Three-Dimensional Analyte-Sensitive Nanostructures and Their Applications. *Chem. Rev.* **2014**, *114*, 10654–10696. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Fuchs, Y.; Kunath, S.; Soppera, O.; Haupt, K.; Mayes, A.G. Molecularly Imprinted Silver-Halide Reflection Holograms for Label-Free Opto-Chemical Sensing. *Adv. Funct. Mater.* **2013**, *24*, 688–694. [\[CrossRef\]](#)
8. Kowalski, B.A.; McLeod, R.R. Design concepts for diffusive holographic photopolymers. *J. Polym. Sci. Part B Polym. Phys.* **2016**, *54*, 1021–1035. [\[CrossRef\]](#)
9. Lin, Y.; Harb, A.; Lozano, K.; Xu, D.; Chen, K.P. Five beam holographic lithography for simultaneous fabrication of three dimensional photonic crystal templates and line defects using phase tunable diffractive optical element. *Opt. Express* **2009**, *17*, 16625–16631. [\[CrossRef\]](#)
10. Lynn, B.; Blanche, P.-A.; Peyghambarian, N. Photorefractive polymers for holography. *J. Polym. Sci. Part B Polym. Phys.* **2013**, *52*, 193–231. [\[CrossRef\]](#)

11. Rahmouni, A.; Bougdid, Y.; Moujdi, S.; Nesterenko, D.V.; Sekkat, Z. Photoassisted Holography in Azo Dye Doped Polymer Films. *J. Phys. Chem. B* **2016**, *120*, 11317–11322. [\[CrossRef\]](#)
12. Bianco, A.; Bertarelli, C.; Castagna, R.; Pariani, G.; Zanutta, A. Photo-chromic materials for holography: Issues and constraints. In Proceedings of the Practical Holography XXVI: Materials and Applications, San Francisco, CA, USA, 21–26 January 2012; Volume 8281, p. 3.
13. Cheben, P.; Belenguer, T.; Núñez, A.; Del Monte, F.; Levy, D. Holographic diffraction gratings recording in organically modified silica gels: Erratum. *Opt. Lett.* **1997**, *22*, 193. [\[CrossRef\]](#)
14. Carretero, L.; Murciano, A.; Blaya, S.; Ulibarrena, M.; Fimia, A. Acrylamide-N,N'-methylenebisacrylamide silica glass holographic recording material. *Opt. Express* **2004**, *12*, 1780–1787. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Ramos, G.; Alvarez-Herrero, A.; Belenguer, T.; Del Monte, F.; Levy, D. Shrinkage control in a photopolymerizable hybrid solgel material for holographic recording. *Appl. Opt.* **2004**, *43*, 4018–4024. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Schnoes, M.G.; Dhar, L.; Schilling, M.L.; Patel, S.S.; Wiltzius, P. Photopolymer-filled nanoporous glass as a dimensionally stable holographic recording medium. *Opt. Lett.* **1999**, *24*, 658–660. [\[CrossRef\]](#)
17. Velasco, A.V.; Hernández-Garay, M.P.; Calvo, M.L.; Cheben, P.; Del Monte, F. Photopolymerizable glasses incorporating high refractive index species and ionic liquid: A comparative study. *J. Appl. Phys.* **2011**, *109*, 53106. [\[CrossRef\]](#)
18. Del Monte, F.; Martínez, O.; Rodrigo, J.A.; Calvo, M.L.; Cheben, P. A Volume Holographic Sol-Gel Material with Large Enhancement of Dynamic Range by Incorporation of High Refractive Index Species. *Adv. Mater.* **2006**, *18*, 2014–2017. [\[CrossRef\]](#)
19. Cheben, P.; Calvo, M.L. A photopolymerizable glass with diffraction efficiency near 100% for holographic storage. *Appl. Phys. Lett.* **2001**, *78*, 1490–1492. [\[CrossRef\]](#)
20. Murciano, A.; Blaya, S.; Carretero, L.; Madrigal, R.F.; Fimia, A. Holographic reflection gratings in photopolymerizable solgel materials. *Opt. Lett.* **2006**, *31*, 2317–2319. [\[CrossRef\]](#)
21. Kuo, C.-Y.; Hsu, T.-C.; Su, W.-H. A facile sol-gel synthesis of crack-free photopolymerizable silica for holographic recording. *J. Non Cryst. Solids* **2012**, *358*, 735–740. [\[CrossRef\]](#)
22. Chang, Y.M.; Yoon, S.C.; Han, M. Photopolymerization of aromatic acrylate containing phosphine oxide backbone and its application to holographic recording. *Opt. Mater.* **2007**, *30*, 662–668. [\[CrossRef\]](#)
23. Su, Z.; Huang, S.; Wang, Y.; Ling, H.; Yang, X.; Jin, Y.; Wang, X.; Zhang, W. Robust, high-barrier, and fully recyclable cellulose-based plastic replacement enabled by a dynamic imine polymer. *J. Mater. Chem. A* **2020**, *8*, 14082–14090. [\[CrossRef\]](#)
24. Tan, X.; Rodrigue, D. A Review on Porous Polymeric Membrane Preparation. Part I: Production Techniques with Polysulfone and Poly (Vinylidene Fluoride). *Polymers* **2019**, *11*, 1160. [\[CrossRef\]](#)
25. Smirnova, T.; Sakhno, O. A mechanism of the relief-phase structure formation in self-developing photopolymers. *Opt. Spectr.* **2001**, *3*, 126–131. [\[CrossRef\]](#)
26. Gul, S.-E.; O'Neill, L.; Cassidy, J.; Naydenova, I. Modified Surface Relief Layer Created by Holographic Lithography: Application to Selective Sodium and Potassium Sensing. *Sensors* **2019**, *19*, 1026. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Birabassov, R.; Galstian, T.V.; Dechamplain, F.; Ritcey, A.-M.R. Azo-dye-doped cellulose acetate for optical data storage and processing. *Proc. SPIE* **1998**, *3491*, 704–709.
28. Wang, K.; Guo, L.; Zhou, L.; Zhu, J. Imaging mechanism of the holographic recording material dichromated cellulose triacetate. *Appl. Opt.* **1996**, *35*, 6369–6374. [\[CrossRef\]](#)
29. Mikulchyk, T.; Walshe, J.; Cody, D.; Martin, S.; Naydenova, I. Humidity and temperature induced changes in the diffraction efficiency and the Bragg angle of slanted photopolymer-based holographic gratings. *Sens. Actuators B Chem.* **2017**, *239*, 776–785. [\[CrossRef\]](#)
30. Kaiser, A.; Stark, W.J.; Grass, R.N. Rapid Production of a Porous Cellulose Acetate Membrane for Water Filtration using Readily Available Chemicals. *J. Chem. Educ.* **2016**, *94*, 483–487. [\[CrossRef\]](#)
31. Rezaei, A.; Nasirpour, A.; Fathi, M. Application of Cellulosic Nanofibers in Food Science Using Electrospinning and Its Potential Risk. *Compr. Rev. Food Sci. Food Saf.* **2015**, *14*, 269–284. [\[CrossRef\]](#)
32. Hariharan, P. *Optical Holography: Cambridge Studies in Modern Optics 2*; Cambridge University Press: Cambridge, UK, 1986; p. 319.
33. Kogelnik, H. Coupled Wave Theory for Thick Hologram Gratings. *Bell Syst. Tech. J.* **1969**, *48*, 2909–2947. [\[CrossRef\]](#)
34. Mikulchyk, T.; Martin, S.; Naydenova, I. N-isopropylacrylamide-based photopolymer for holographic recording of thermosensitive transmission and reflection gratings. *Appl. Opt.* **2017**, *56*, 6348–6356. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Leite, E.; Naydenova, I.; Mintova, S.; Leclercq, L.; Toal, V. Photopolymerizable nanocomposites for holographic recording and sensor application. *Appl. Opt.* **2010**, *49*, 3652–3660. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Yetisen, A.K.; Butt, H.; Volpatti, L.; Pavlichenko, I.; Humar, M.; Kwok, S.J.; Koo, H.; Kim, K.S.; Naydenova, I.; Khademhosseini, A.; et al. Photonic hydrogel sensors. *Biotechnol. Adv.* **2015**, *34*, 250–271. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Jiang, N.; Butt, H.; Montelongo, Y.; Liu, F.; Afewerki, S.; Ying, G.; Dai, Q.; Yun, S.-H.; Yetisen, A.K. Laser Interference Lithography for the Nanofabrication of Stimuli-Responsive Bragg Stacks. *Adv. Funct. Mater.* **2017**, *28*, 1702715. [\[CrossRef\]](#)