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Research on Holographic Sensors and Novel Photopolymers at the Centre for Industrial and Engineering Optics

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1. Introduction

The recent resurgence of interest in photopolymers for commercial holograms is a strong incentive for development of photopolymers that are as environmentally friendly as possible. Photopolymer materials consist of a light-sensitive film which is exposed during production to form the hologram, thereby offering versatility well beyond that of current security holograms, which are mass produced from a master using a foil stamping processes.

Most holographic recording media based on photopolymerizable materials contain monomers such as acrylates or acrylamides as well as an electron donor such as Triethanolamine, a light absorbing dye such as Methylene Blue or Erythrosine B and an inert polymer binder such as Polyvinyl Alcohol.

Like their foil-stamped/embossed counterparts, the finished photopolymer hologram is a thin, solid layer applied to the surface of a product or package and any harmful monomers present in the photosensitive recording material have usually been fully polymerized during the exposure/recording process. Even so, the handling of raw materials during mass production and the disposal of waste produced by the production process must be carefully controlled when harmful monomers are present. Replacement of the current monomers with environmentally friendly constituents is better for the environment and may help to reduce overall production cost.

Photopolymers have been in development since the late 1960s, but development of the embossing technique for mass production of surface relief holograms in the early 1980s led to

commercial success for the now familiar surface hologram. Since the early work of Close et al. [1] some photopolymers for holography have been produced commercially. The well known DuPont photopolymer [2-4] and Polaroid DMP-128 [5, 6] emerged in the 1970's and 1980's but commercial use was limited.

As interest in holographic data storage grew, Polaroid spin-out company Aprilis began to commercialize their material, and the Bell Laboratories spin out company, InPhase introduced the new 'Tapestry' medium for holographic data storage. General Electric were also developing a data storage medium.

Currently, the biggest market in commercial holography is security holograms. However, despite the growth in activity in volume materials for data storage, until very recently the security hologram industry focussed almost exclusively on surface relief holograms. Over the last five years we have seen significant activities in developing of volume photopolymer holograms. DuPont has been joined by other large commercial companies including Bayer [7, 8] and Sony [9] in offering commercial holographic photopolymer materials to industry. With the prospect of very high volume production, environmental and cost considerations become even more important.

The photopolymer phase reflection hologram is attractive for security holograms for a number of reasons. The fact that it is relatively thick by hologram standards (tens of microns) means the diffraction efficiency can be very high, leading to eye-catching 3D images, visually quite different to the rainbow effect of the embossed hologram. A second important feature of the photopolymer reflection holograms is the capacity to angularly multiplex several holograms into one layer. In photopolymers with high refractive index modulation, this can produce a moving image effect, which is very striking. Even a small number of multiplexed holograms can enable toggling between two static images, so that text or warnings can be visible in conjunction with the holographic image. A third beneficial characteristic is the broad range of wavelength sensitivity in many photopolymers [10–12], enabling several colour components in the hologram. Finally, most photopolymers are completely self developing and require no chemical processing. This means that they can be exposed individually during production thus introducing the possibility of serialization and individualized data [12, 13] to provide a new level of security.

As well as improving the polymer formulation, this Chapter aims to illustrate some properties, unique to volume photopolymer holograms, that could be developed into innovative products. In a recent overview at HoloPack-HoloPrint 2012, Lancaster and Tidmarsh pointed out that the security market is one of the main drivers for growth and innovation in the industry and the market is changing as customers are demanding more functionality in security technologies [14].

This chapter is divided in two parts. The first part describes some attractive applications of an acrylamide-based photopolymer developed in the Centre for Industrial and Engineering Optics (IEO), at Dublin Institute of Technology. This particular photopolymer is characterised by high diffraction efficiency and self development (immediate) [15], and it can be prepared in thickness ranging from a few microns to 1mm [16]. It has been recently reformulated for

panchromaticity [10] and improved with the addition of nanoparticles [17-22]. This holographic photopolymer is sensitive to humidity [23-26] and to high pressure. It was discovered recently that its pressure sensitivity can be varied using a particular additive and adjusting the polymer's chemical composition accordingly. The second part of the chapter reports results for a novel photopolymer based on diacetone-acrylamide.

2. IEO Holographic sensor technology

Research in IEO has been focused on holography and its applications using, mainly, low cost photopolymers which are water soluble and require no chemical or other form of processing. IEO is one of very few places in the world capable of making acrylamide photopolymer reflection holograms that can be viewed in ordinary light, like the holograms on credit cards. Until recently this was not possible, but IEO researchers have overcome the technical problems.

Holograms are made by exposing the photopolymer film to two beams of coherent laser light. When the finished hologram is illuminated at the playback or reconstruction stage by just one of the beams, the second beam reappears. This is how holographic images are produced. If the second beam was originally reflected from an object before reaching the film then, on reconstruction we'd see an image of the object. Furthermore if the two beams approach the film from opposite sides, the hologram can be played back in white light in which case we'd see a holographic image in the colour of the laser light that was used for the recording. Such holograms are known as reflection holograms. If no object is used and both recording beams illuminate the film directly then we obtain what's known as a holographic grating because the pattern of light formed at the film by the interference of two beams consists of finely spaced bright and dark regions and the recording consists correspondingly of finely spaced regions of photo-polymerised material interspersed with unpolymerised material.

Holographic sensors of three types are under development, both offering a number of advantages including visual, easy interpretation of information by non specialists, low cost, flexible design and small format.

In the first type of sensor a change in the dimensions, or average refractive index or refractive index modulation occurring in the photopolymer layer, when it is exposed to an analyte will cause the brightness or, in the case of a reflection hologram, the colour of the reconstructed light to change. Holographic indicators that change colour when exposed to a change in relative humidity have been developed [23-26]. The device can be calibrated so that a precise reading of the colour enables an accurate measure of relative humidity. The pictures in Fig. 1 show the change from blue to red in the colour of the reconstructed image from a hologram after it is simply breathed on. The colour reverts to the original after a few minutes.

The humidity sensitive hologram may alternatively be used as a security device. Holograms are a common feature on credit cards, banknotes, passports, concert tickets and other high value items and are put there as an authentication device. However it has become fairly easy to counterfeit these mass produced holograms. IEO's new humidity sensitive holograms are particularly difficult to emulate and can be used to provide an added level of authentication.



Figure 1. Moisture sensitive colour changing hologram

The second type of sensor relies on a very simple principle. Polymerisation by visible light requires that the monomers, a co-initiator and a sensitizer all be present in order for photopolymerisation to take place. If the sensitizer is absent then photopolymerisation is impossible.

Because the presence of the dye is essential, the film is usually made sensitive to light during its preparation. Here we separate the film preparation and the sensitisation processes (Fig. 2). In this way the photo-polymerisation process is used to detect dye labelled analytes, providing an alternative to fluorescence detection methods.

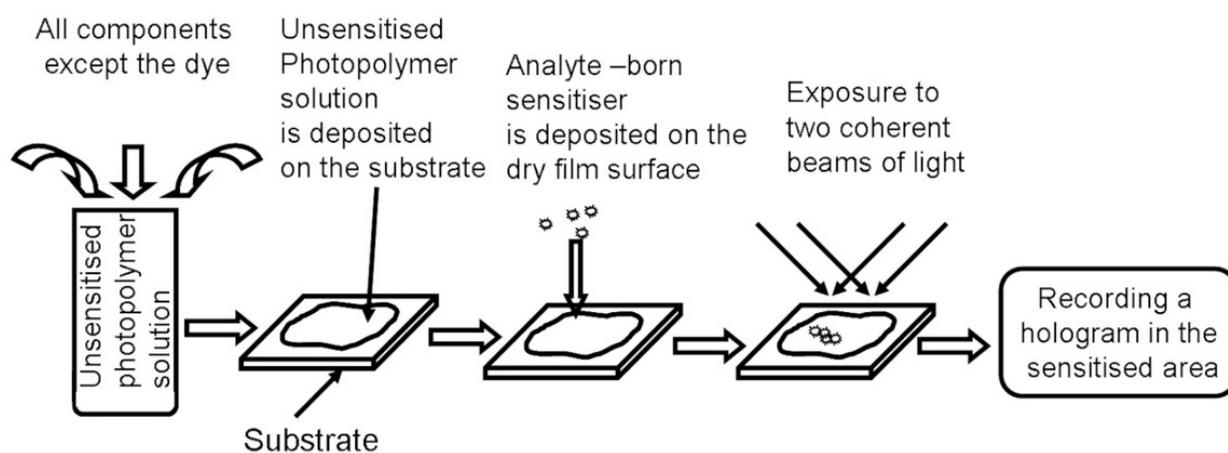


Figure 2. Detection principle based on novel approach to photopolymer sensitisation

We have been successful in the detection of dye-labelled DNA single strand molecules by the recording of a simple holographic grating (Fig.3) [27]. The minimum amount of material that has been detected was $5 \cdot 10^{-14}$ mol.

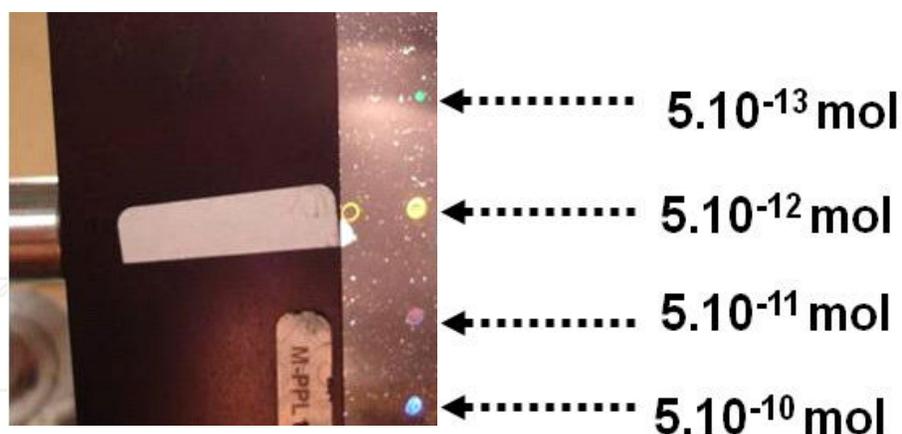


Figure 3. Holographic gratings recorded in photopolymer layer deposited on top of dye-labelled DNA molecules immobilised on a substrate. Arrows indicate areas in contact with dye-labelled DNA exposed to holographic recording

The significance of the principle described above extends beyond holographic sensing. It opens new possibilities in optical device fabrication [27]. Figure 4 shows a Fresnel lens made in this way. The sensitiser was deposited in the pattern of the required device on a photopolymer film, which was then exposed to ordinary light.

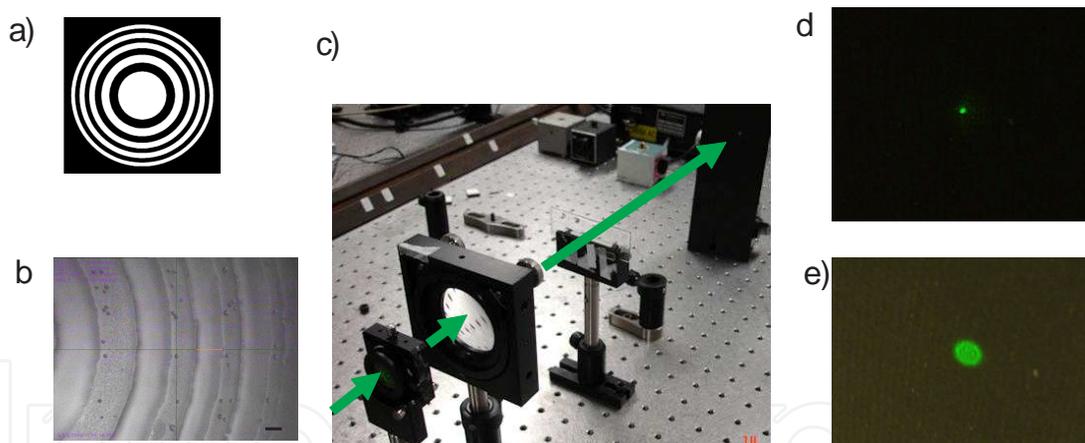


Figure 4. a) Fresnel lens pattern b) deposited sensitiser pattern on photopolymer film c) demonstration experiment using a collimated beam of laser light d) focussed spot with Fresnel lens in place e) lens removed

The third type of sensor is a pressure sensor. A pressure sensitive photopolymer (PSP) for tactile pressure measurements and their colour visualisation was developed recently in IEO. This pressure sensitive material is cheap and easy to produce. Its chemical composition is similar to the standard IEO holographic photopolymer [15-16]. This optimised photopolymer is capable of recording transmission and reflection holograms. The reflection holograms recorded in this novel material are of particular interest for different applications (Fig. 5), because of their ability to produce colour maps of pressure distribution without the need for scanning and digital processing.



Figure 5. Applications requiring a thin film capable of tactile pressure measurements

The operating principle (Fig. 6) is that the colour of the reconstructed light from a reflection hologram, illuminated by ambient light, depends on the pressure to which the hologram has been subjected. This principle derives from the fact that the hologram is made in an elastic photopolymer, which compresses under pressure, in turn reducing the recorded interference fringe spacing and hence the resonant wavelength of the device.

When a reflection hologram is illuminated with white light, light of a specific colour is diffracted and this is the colour observed. If a red laser is used for recording of the reflection hologram the reconstructed image will be observed in red.

Pressure sensitive photopolymers shrink due to applied pressure, which leads to a change in the fringe spacing of the hologram, and consequently to change in the colour observed (Fig. 6). The colour changes from red to yellow – green – blue as the applied pressure increases.

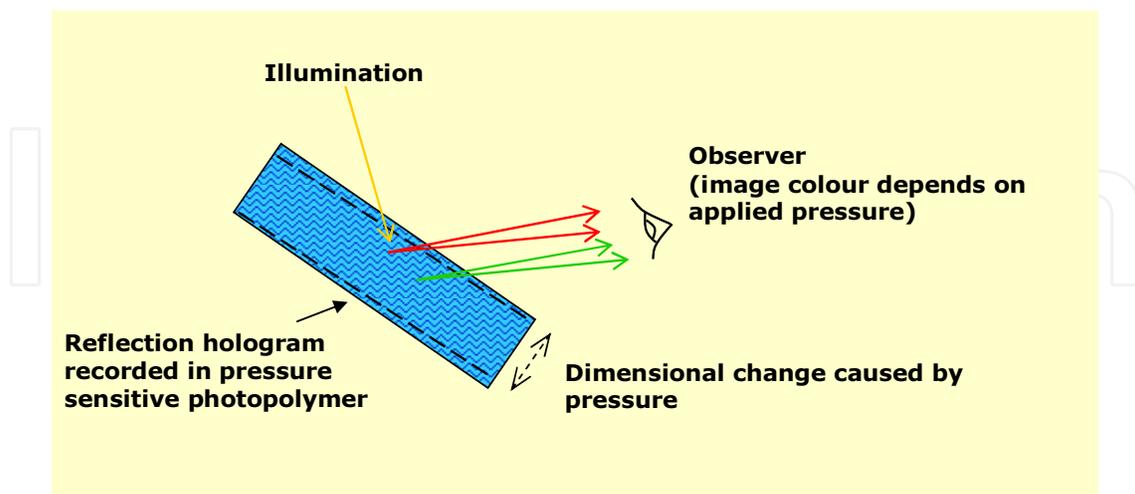


Figure 6. Principle of operation of a holographic pressure sensor

As a first step in the development of a new family of holographic sensors, several photopolymer compositions with different pressure sensitivities were produced. The initial tests

performed with an INSTRON machine show that that the reconstructed images from reflection holograms made in the new PSP material, change colour when pressure is applied. Four different compositions were investigated (PSP1, PSP2, PSP3 and PSP4). Figure 7 and Figure 8 show our results for the pressure sensitivity of different PSPs. Figure 7 presents results for one PSP composition (PSP3) under two different applied pressures.

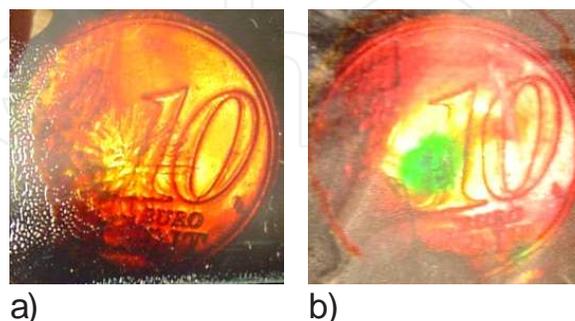


Figure 7. Change in hologram colour in thin films of PSP3 photopolymer under pressure of: a) 10 N/cm²; b) 50 N/cm²

Figure 8 present results for one pressure applied to thin films of three different PSP compositions. The results are repeatable and can serve as a basis for development of pressure sensitive thin film material with tuneable pressure sensitivity.

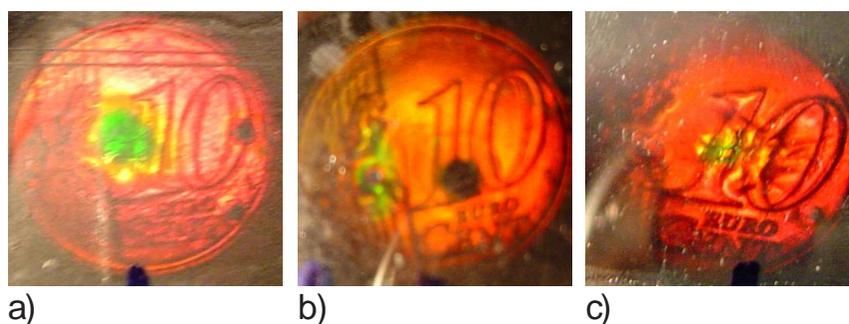


Figure 8. Change in hologram colour under pressure of 80 N/cm² in photopolymer thin films of: a) PSP1; b) PSP2, c) PSP4

The pressure sensitivity of the photopolymers diminishes in the direction (highest) PSP2 ⇒ PSP1 ⇒ PSP4 (lowest). The object in all experiments was a 10 cent coin for display purposes.

3. Environmentally friendly holographic photopolymers

The suitability of PVA/Acrylamide photopolymer materials for holographic applications is currently a hot research topic under investigation by numerous research groups [20-33]. However the toxicity of these photopolymer materials is of concern. This toxicity can be attributed to the carcinogenic nature of the monomer acrylamide (AA) [34-37]. As holographic

technologies are advanced, there is going to be a need for recording media, which can be produced in bulk with little risk to workers involved in its manufacture or to the environment. In order for photopolymer recording media to be a viable option for holographic applications, this issue has to be addressed, and a replacement monomer must be used.

Research into the development of non-toxic, water-soluble photopolymers has been reported by Ortuno et al. [38-40]. Sodium Acrylate (NaAO) was chosen as the substitute monomer in the photopolymer composition, the toxicity of which is reported to be lower than AA [41]. A maximum diffraction efficiency of 77% at the Bragg is reported for 900 μm thick NaAO photopolymer layers [38] at a spatial frequency of 1125 l/mm, with a recording intensity of 5mW/cm². A refractive index modulation of $\sim 2.24 \times 10^{-4}$ is reported for the NaAO photopolymer. This is a factor of a magnitude lower than the refractive index modulations achieved with the PVA/AA composition [15, 28, 42]. This could be partly due to the difference in the refractive index of the AA and NaAO based materials [39]. The shrinkage of the NaAO photopolymer has been measured at $\sim 3\%$, making it unsuitable for data storage applications.

A low toxicity water-soluble material using PVA photosensitized with dihydrated copper chloride ($\text{CuCl}_2(2\text{H}_2\text{O})$) is reported by Olivares-Perez et al. [43]. An attractive feature of this material is its ability to conduct electricity, making it a candidate for opto-electronic applications. However the maximum diffraction efficiency recorded in 200 μm thick layers in transmission mode is very low, 3.9%.

IEO has developed a new non-toxic photopolymer using the monomer Diacetone Acrylamide (DA) as the replacement for AA. A cytotoxicity comparison of the two monomers has been carried out. The replacement of AA with DA is justified by a decrease by two orders of magnitude in the Lethal Dose, or LD50, concentration. The results of this study will be published elsewhere. Characterisation of the holographic recording capabilities of the water-soluble material in the transmission mode of recording has been carried out [44]. Diffraction efficiencies greater than 90% were obtained in 80 μm layers at 1000 l/mm, and a refractive index modulation of 3.3×10^{-3} has been obtained. This compares favourably to the refractive index modulation achievable with the AA-based photopolymer, as shown in Fig. 9. The DA photopolymer demonstrates a more uniform trend in intensity dependence than the AA photopolymer, which is most likely due to the larger monomer molecule size. As the rate of polymerisation is increased, the refractive index modulation for DA levels out due to a reduced rate of diffusion. This can be compared to the smaller AA monomer molecules which are more easily able to diffuse at higher recording intensities, and therefore the maximum refractive index modulation is greater. The DA photopolymer has also been doped with different additives, such as glycerol, which improves both the optical quality of the layers and its response at low exposure energies [45, 46]. Theoretical models [42] are currently being modified to explain the behaviour of the new non-toxic photopolymer. Initial Raman spectroscopy studies indicate that the mechanism for photo-polymerisation is the same for the DA and AA monomers, as the double peak observed at $\sim 1630\text{cm}^{-1}$ for DA and the cross-linker bisacrylamide (BA) matches that observed for AA and BA (Figures 10, 11) [47].

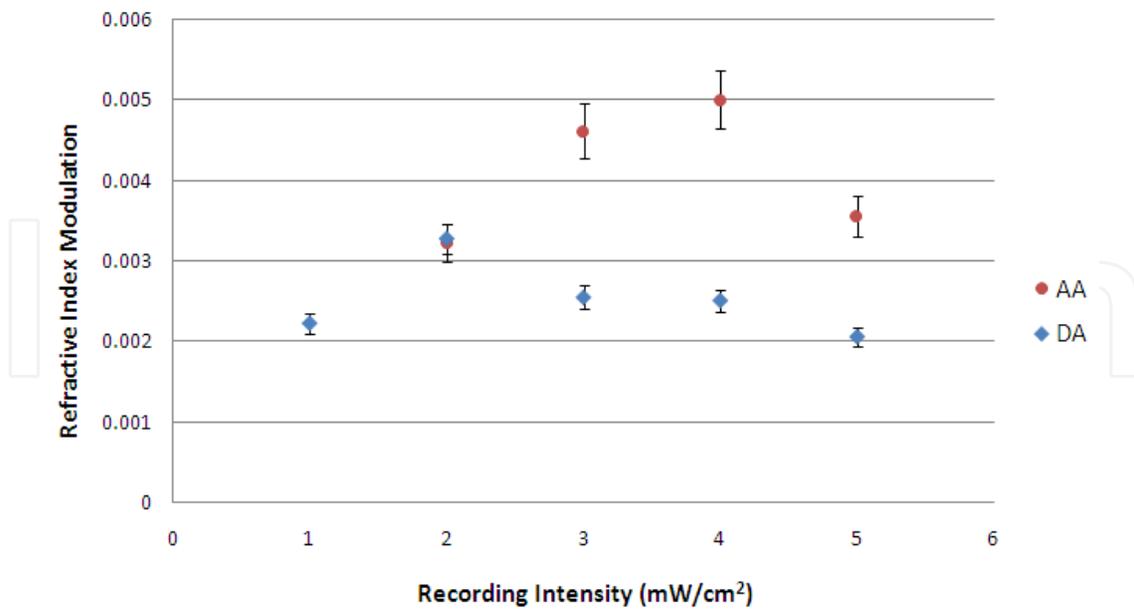


Figure 9. Refractive index modulation vs. recording intensity for the DA and AA photopolymers at 1000 l/mm with an exposure energy 100mJ/cm².

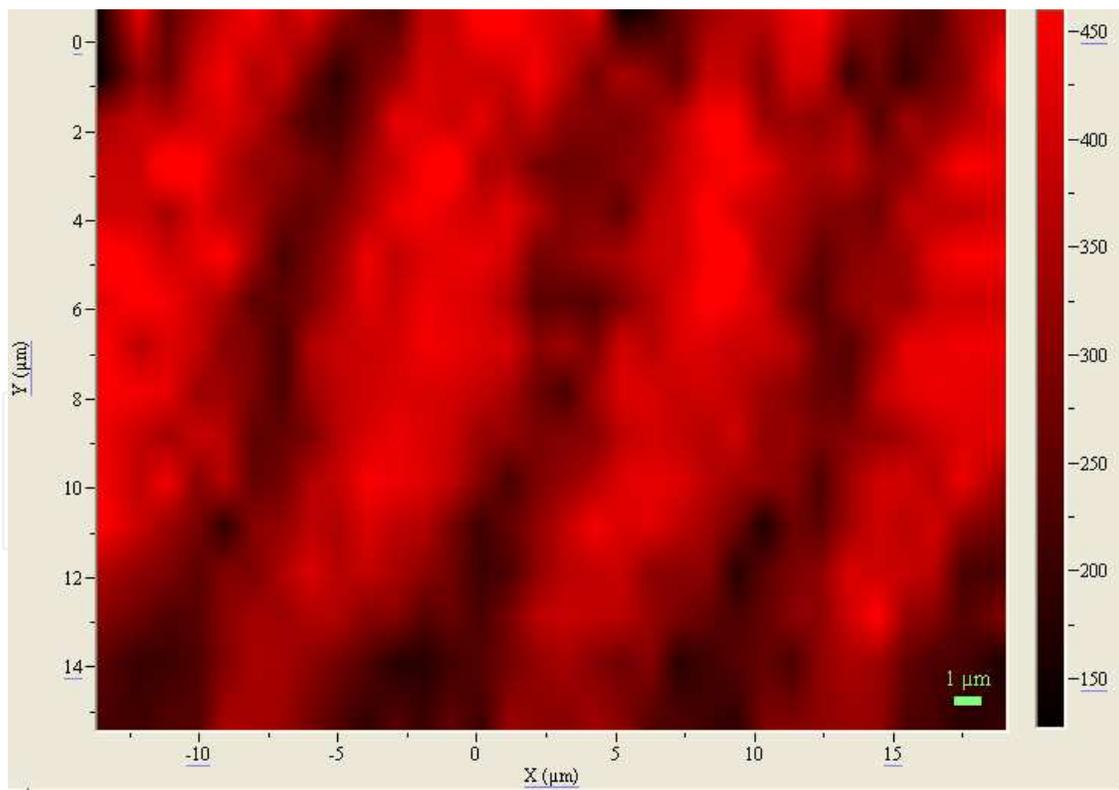


Figure 10. Raman map showing the redistribution of the 1636cm⁻¹ DA peak across a holographic grating with a fringe spacing of 10μm, recorded in the DA photopolymer. Measurements were taken at 514nm with a S.A. (Jobin Yvon) LabRam 1B Spectrometer.

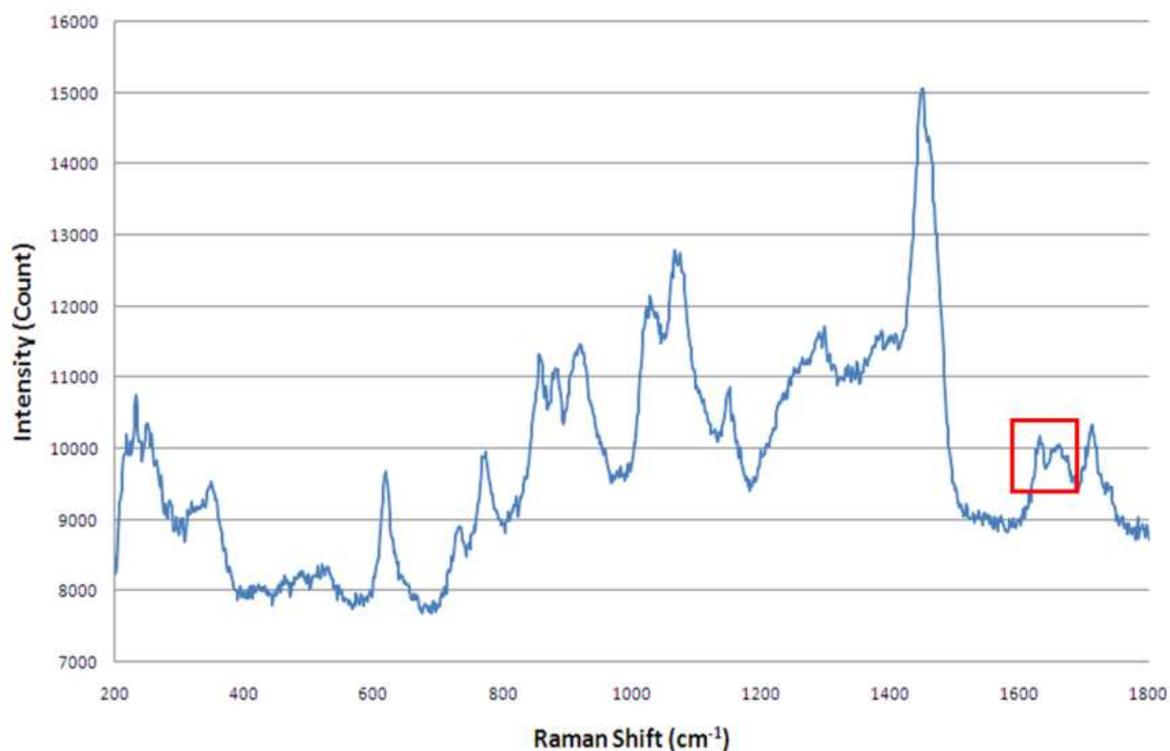


Figure 11. Raman spectrum of the DA photopolymer taken from the map in fig. 2. The peaks at 1636 cm⁻¹ and 1658 cm⁻¹ (shown in the red box) correspond to the DA and BA C=C bonds respectively.

4. Conclusion

The chapter reviewed recent developments in holographic sensors technology at the Centre for Industrial and Engineering Optics (IEO) at Dublin Institute of Technology. We also reported the development of a novel environmentally friendly holographic photopolymer. Acrylamide is excluded from the composition of this photopolymer. Diffraction efficiencies greater than 90% are achievable in 80 μ m layers at 1000 l/mm, and a refractive index modulation of 3.3×10^{-3} has been obtained. This compares favourably to the refractive index modulation achievable with the acrylamide-based photopolymer. Characterisation of the recording capabilities of the diacetone-based photopolymer in the reflection mode of recording will follow.

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