Photochromic polyurethanes for rewritable CGHs in optical testing

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Abstract: The development of photochromic Computer Generated Holograms (CGHs) to test any complex optics, such as aspheres and free-form optics, is described. A thermally irreversible photochromic polyurethane has been synthesized to give good thin films with a strong modulation of the optical transmission. The photochromic CGH has been tested with a simple interferometrical configuration showing promising results. The use of photochromic CGHs provides advantages over standard technologies, as rewritability and self developing.

OCIS codes: (090.2890) Holographic optical elements; (120.3180) Interferometry; (160.5335) Photosensitive materials; (160.5470) Polymers; (220.1250) Aspherics; (220.4840) Testing.

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Materials showing switchable optical properties are interesting in developing smart devices. In this framework, photochromic materials are one of the most studied classes, since their properties can be conveniently triggered by photoirradiation [1,2]. The color change is the eye-sighted consequence of a change in the UV-Vis absorption spectrum. Photochromism has been applied in sunglasses and inks for textiles, and it has been studied for optical memories and switches [3–6] and holographic optical elements [7–16].

Nowadays, very complex and precise optical surfaces are produced over a wide range of dimensions, as well as aspheric or free-form optics, that are currently used in cameras, objectives and telescopes [17]. As a matter of fact, null interferometry [18], which is the most important technique used in this field, performs a rapid measurement of the entire surface of test element. Aspherical optics make more challenging the optical metrology in comparison with spherical elements, since they require non standard reference surfaces. In this background, a possibility lies in Computer Generated Holograms [19–22], which reproduce the wavefront of the test optics by an amplitude or phase pattern on a flat or spherical surface. At present, intensity CGHs are made in chrome on glass substrates, using technologies developed for the microelectronic industry, such as laser-beam or electron-beam recording.

The strong change in transparency between the two light-induced states makes photochromic materials an attractive possibility to develop new-concept CGHs. The reversibility of the photochromic process would impart re-writability to the device, thus enabling to write and erase different holograms according to the requests. Moreover, the production of photochromic CGHs requires only two steps: *i)* the film processing to give a high quality photochromic layer, in terms of homogeneity, flatness, abrasion and optical contrast, and *ii)* the optical writing of the pattern. No development process, which is usually carried out with commercial products using photoresists, is needed.

As the written pattern has to be stable over the interferometric test, thermally irreversible photochromic systems are required and, among them, 1,2 dithienylperfluorocyclopentenes (DTEs) have been considered. Indeed, from the cis-stilbene [23] the basic diarylethene structure have been modified to yield DTEs showing P-type photochromism, with excellent response in terms of sensitivity and fatigue resistance [24–26]. Moreover, the position of the absorption band in the visible can be conveniently tuned by acting on the chemical structure, namely by introducing additional aryls and/or electro-active substituents at the 5-5′ positions of the thiophenes [27–30]. To be used in optical devices, photochromic molecules have to be processed to yield amorphous materials. Doping an amorphous polymer matrix is not enough to obtain a strong change of the optical properties, since the content of photochromic molecules must be maintained low to prevent the formation of aggregates. Bonding the photochromic molecules through polymerization [31–38] or sol-gel processes [39,40] offers the possibility to significantly increase the amount of chromophores. For both methods, the DTEs has to bear side-groups suitable to react with the other chemical species.

For this study we referred to polyurethanes as their versatile chemistry allows to conveniently address the material properties, according to the requests. Generally speaking, polyurethanes are produced by polymerization of a diisocyanate and a polyol, the latter being used as soft spacer. To synthesize photochromic polyurethanes, 1,2 bis-(2-methyl 4-(*p*-hydroxymethylphenyl)-3-thienyl) perfluorocyclopenthene (DTE-CH_2OH) [41] (λ_{max} = 584 nm; $\varepsilon = 1.64 \pm 0.05 \cdot 10^4$ $M^{-1}cm^{-1}$ in ethanol) was polymerized with the 4,4'-diisocyanate dicyclohexylmethane (H_{12}MDI). Moreover, polycaprolactone diole and triol were added in order to provide suitable mechanical properties to the films. The relative quantity between the DTE-CH_2OH and the polycaprolactone diole was varied, maintaining the overall stoichiometry with the diisocyanate, and the photochromic content has been increased up to 50% *w/w*. The reaction was catalyzed by the organometallic compound dibutyltin dilaurate (DBTL) and the tertiaryamine 1,4-diazabicyclo[2.2.2]octane (DABCO). Once mixed all the reactants, the batch was directly processed by spin coating or casting assisted by a control coater (Doctor blade technique) to form films through an in situ polymerization. The polymerization has been completed at 130°C for about eight hours. The general formula of the photochromic polyurethane is sketched in Fig. 1. As the application we aimed at calls for severe requirements in the overall optical quality of the films, TEGO® Glide 440 was added to the reaction batch to support the spreading of the solution onto the glass substrates (n-BK7).

The flatness of the surface can be easily measured, using a Fizeau interferometer. Figure 2 shows the interferometric measurement of a photochromic film on a n-BK7 substrate (30 mm in diameter, λ/4 PV surface flatness) obtained by spin coating. On a 15 mm diameter subaperture, a surface quality of λ/2 PV and λ/10 RMS values has been reached, which is a clear evidence of the goodness of the specimen. This means that the photochromic film almost preserve the optical quality of the glass substrate.

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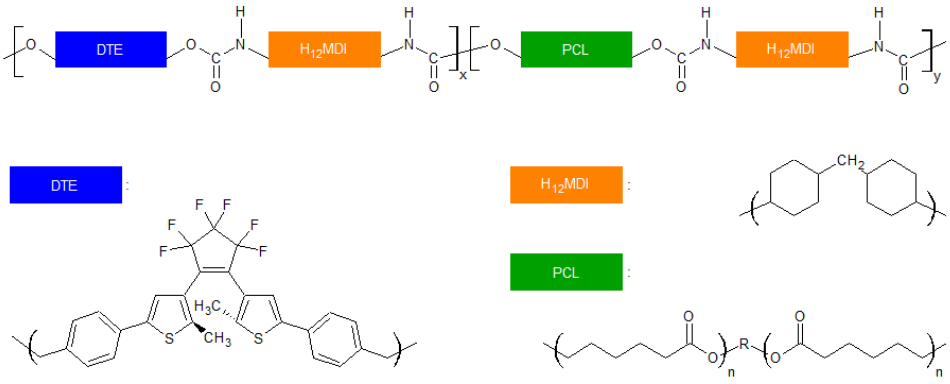

Fig. 1. The random photochromic copolymer.

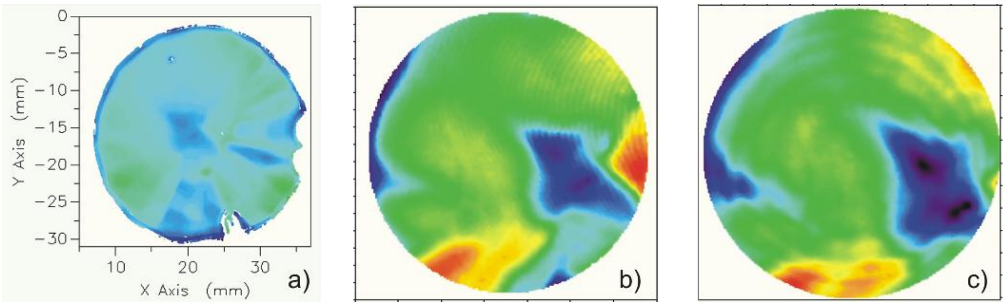

Fig. 2. a) Interferogram of a 4 µm thick, 50% w/w DTEs content photochromic film on a n-BK7, 30 mm, λ/4 PV substrate (PV: 990 nm, RMS: 112 nm). Particular of a 15 mm diameter subaperture b) before the pattern application (PV: 250 nm, RMS: 44 nm) and c) after the pattern application (PV: 243 nm, RMS: 43 nm).

The transmittance spectra (Fig. 3) clearly show that the produced films are completely transparent in between 800 and 2500 nm (only the reflection losses are present) for both colored and colorless forms, without any indication of light scattering. This confirms the overall optical quality of the substrates. At shorter wavelengths (500-700 nm) the change in transmittance can be quantified by introducing the contrast parameter (C), as follows:

$$C(\lambda)=\frac{T_{colorless}(\lambda)}{T_{colored}(\lambda)}\approx 10^{A_{colored}(\lambda)} \qquad (1)$$

The contrast is a function of the wavelength and it is driven by the transmittance of the colored form, since the transmittance of the colorless form is close to 1. The absorbance (A) is related to the molecular structure of the photochromic dye through the absorption coefficient (ε) and to the optical path that is, at the solid state, the film thickness (Z):

$$A(\lambda)=\varepsilon(\lambda)\cdot Z \qquad (2)$$

The absorption coefficient, which also depends on the wavelength and on the concentration of the photochromic units into the film, is a figure of merit of the photochromic molecule considered. Its value is calculated, knowing the molar mass of the photochromic dye M_{ph} (g/mol), its concentration in the film $w_{\%}$, the absorption coefficient of the pure photochromic material ε' (m^{-1}) and the density ρ (g/m^3) of the film, according to the following equation:

$$\varepsilon(\lambda)=\frac{100\cdot M_{ph}\,\varepsilon'(\lambda)}{\rho\, w_{\%}} \qquad (3)$$

In Fig. 4a the absorption coefficient for a film in the colored and colorless forms is reported in the UV-Vis region. In the range 500-700 nm, the colored form shows a large

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absorption coefficient, which reaches values up to 1.1 μm^{-1} at 590 nm and 0.7 μm^{-1} at 633 nm for a polyurethane film with a content of dithienylethene of 50% *w/w*. With these values of the absorption coefficient, the contrast value increases of an order of magnitude for each micron of film thickness (Fig. 4b). Large contrasts are required for obtaining efficient CGHs. Indeed considering a binary amplitude Fresnel Zone Plate (50% duty cycle, sharp edges and infinite contrast between opaque and transparent zones) the theoretical diffraction efficiency in the first converging order is 10.1% [42]. Decreasing the contrast results in decreasing the diffraction efficiency to 9.5%, 8.2%, and 4.7% for contrast values of 10^3, 10^2, and 10 respectively. We can set 10^2 as the lower limit for the contrast in photochromic CGHs, therefore films with thicknesses of few microns (2-3 μm with 50% *w/w* of photochromic dye) are enough to reach good performances.

Once fixed the film thickness and the content of the diarylethene monomer units, the irradiation time has to be determined to reach the maximum conversion between the two states, that is the maximum contrast. As both isomer forms have high absorption coefficients in the UV, the kinetics of the photoinduced process slows while the colored form is formed. For example, when $\varepsilon_{colored} = \varepsilon_{colorless}$, i.e. at the isosbestic point, the colored thickness of the film grows logarithmically with time [43]. In our case, a film 6 μm thick with a content of photochromic monomer units of 50% *w/w* can be completely triggered into the blue form by a 20’ exposure to a wood lamp ($\lambda = 365$ nm, 2.5 mW/cm^2) on both sides.

A simple custom He-Ne laser plotter was developed to transfer rotationally symmetric Computer Generated Holograms on the photochromic layers. The first test of this new technology dealt with the preparation of CGHs simulating spherical lenses (binary amplitude Fresnel patterns) with different focal lengths.

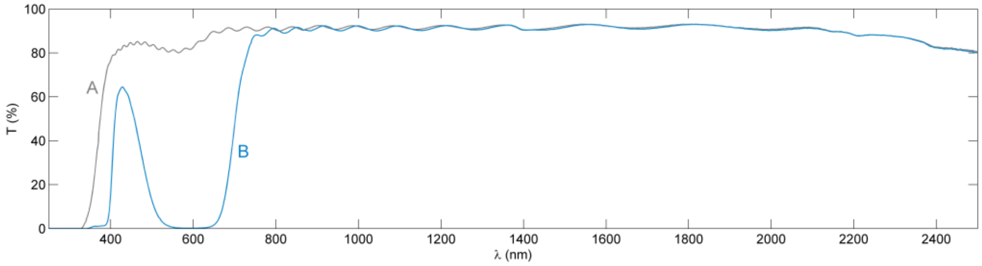

Fig. 3. UV-Vis-NIR spectra of a 4 μm thick film containing 50% w/w DTEs. A: colorless form; B: colored form.

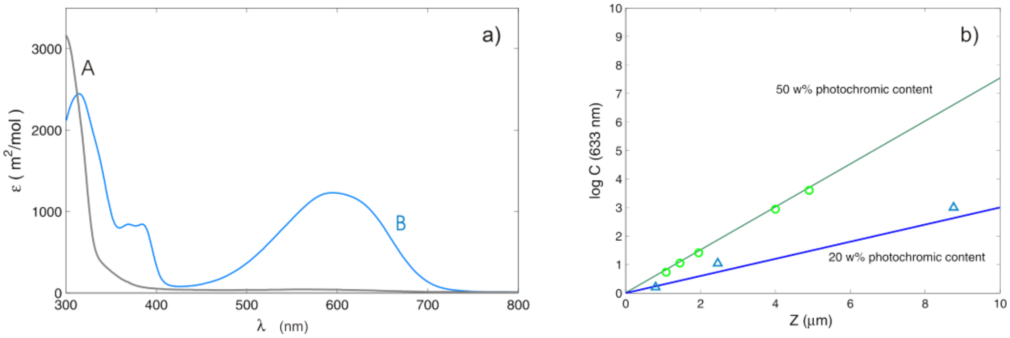

Fig. 4. a) Molar absorption coefficient ε of the photochromic polyurethane in the UV-Vis range of the spectrum. b) Contrast trend at 633 nm as function of film thickness Z for two film series, with different photochromic content (straight lines calculated from ε data; dots are experimental data).

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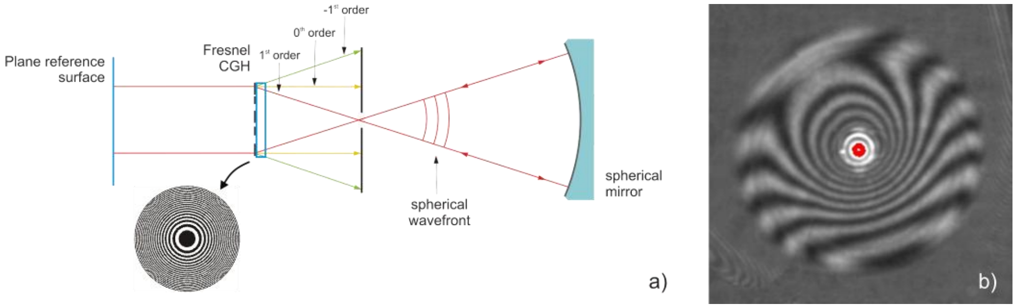

Fig. 5. a) Configuration of the interferometrical test of the Fresnel CGH; b) Recorded fringes.

The configuration of the test is sketched in Fig. 5a, where the photochromic CGH is the optical element under test, that is compared with a reference spherical surface. The reference wavefront is the plane wavefront from a Fizeau interferometer; the photochromic device generates an aberrated converging spherical wavefront in the first diffraction order, which is then reflected back by a reference spherical mirror. Interference fringes result as the difference between the plane reference wavefront and the plane wavefront which is generated by the CGH in double pass. If a perfect spherical wavefront is produced by the CGH, the interference fringes are straight lines, which result from the tilt of the interfering plane wavefronts.

The interference fringes which has been obtained by using a 20 cm focal length photochromic CGH are reported in Fig. 5b. The fringes are well visible, thus indicating that the produced CGH satisfies the basic requirements of optical quality and contrast between opaque and transparent zones. The overall transmission of the CGH was 36.3% and the contrast 200 at 633 nm. The diffraction efficiencies of the zero order and of the first converging order were 30.1% and 9.0% respectively, approaching the theoretical values of 25% and 10.1%; moreover, this values are in agreement with the efficiencies calculated from the measured contrast values.

On the other hand, the fringes are not straight lines, thus indicating that some errors have been introduced somewhere in the production of the photochromic CGH. Error sources in CGHs can be classified in *i)* errors due to the surface flatness and *ii)* errors due to fabrication limitations, as pattern distortions and duty-cycle or each-depth irregularities [44,45]. The flatness of the surface has been measured before (see discussion above) and after the grating patterns are applied to confirm that the surface quality is almost not affected by the writing process. In addition, as the optical writing is the last step in the production of the photochromic CGH, no development process being necessary, we can assert in a good approximation that error sources are limited to pattern distortions. In the case herein discussed, surface values of 3λ PV and λ/2 RMS have been obtained.

Although these results are promising and may represent the proof of concept that the photochromic films can be used to test optical surfaces, in particular aspheres, a high precision writing tool (i.e. laser maskless lithography) is certainly required to improve the performances of the device. Moreover, acting on film quality, further improvements can be achieved. Nevertheless, this approach provides some advantages over standard technologies: as each CGH is specific for any different test surface and test configuration, the photochromic device makes possible to write and erase different patterns on the same substrate according to the requests. The process is simple and the writing tool can be mounted in line with the testing facility.

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