Research Article

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Irradiation of hydrophilic acrylic intraocular lenses by a 365 nm UV lamp

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Abstract: Intraocular lenses (IOLs) based on a transparent hydrophilic acrylic polymer have been irradiated by a 365 nm UV lamp at a 200 mJ/cm^2 fluence and at different exposure times, from 1 h up to 19 h, in air and at room temperature. The macromolecular modifications induced in the lens have been investigated by attenuated total reflectance coupled to Fourier transform infrared spectroscopy and optical spectroscopy. Particular attention was devoted to the study of chemical modifications of the IOL by UV irradiation, which induced chain scissions, radical formation, and cross-links in the more superficial polymer layers. The experimental results at long exposures demonstrate that the IOL transmission decreases in the UV and NIR ranges, remaining nearly constant in the visible range.

Keywords: ATR–FTIR spectroscopy, biomaterials, intraocular lenses, pHEMA, UV irradiation

1 Introduction

Polyhydroxyethyl methacrylate (pHEMA), having the chemical composition $(C_6H_{10}O_3)_n$ [1], with high transparency to visible radiation, is a lightweight polymer biocompatible employed for different applications, such as cell culture flask coatings in microbiology [2], optical couplers and fibers in optics [3], soft contact lenses in ophthalmology [4], and intraocular lenses (IOLs) for cataract surgery [5]. Hydrophobic acrylic lenses have excellent properties, such as superb chemical inertness, optical transparency, relatively high refractive index, and the lowest incidence of posterior capsule opacification (PCO) [6]. pHEMA IOLs have the advantage of being more efficient and functional than those based on PMMA and being foldable, and they can be introduced into the lenticular sac by a small corneal incision that does not require suture-enhancing safety, surgery, and maintenance of the corneal profile [7,8], owing to their high flexibility and high oxygen permeability, facilitating lens positioning and natural cornea oxygenation, and preventing adverse clinical events associated with corneal hypoxia [1]. This low-cost polymer is also employed for bone tissue generation [9], wound healing [10], cancer therapy [11], antimicrobial strategies [1], and for ocular drug delivery [12]. Although pHEMA provides good biocompatibility and stable hydration, having light transmission in the visible region to about 85% [13], it is susceptible to calcification and opacification over time, which can affect long-term visual clarity. This reduction can be compensated by employing other materials or polymers, like silicone or PMMA (polymethylmethacrylate), allowing it to reach values higher than 90% [14,15]. Nevertheless, although the employment of silicone may reduce the risk of PCO, it may introduce optical aberrations and challenges in implantation due to its rigidity [16]. Similar problems are presented by employing PMMA since its employment in IOLs requires larger surgical incisions due to their rigidity, making them less favored in modern practices despite their durability [17].

Thus, being soft and flexible, pHEMA guarantees the comfort of IOL wearers, as opposed to other rigid polymers such as silicone and PMMA.

The first hydrophilic acrylic IOL was implanted in 1983 in Perth, Australia [18]. The mechanical strength of pHEMA-based hydrogels also ensures that soft IOLs are reasonably durable. Recently, ultraviolet (UV)-induced photograph polymerization has been regarded as a simple, fast, efficient, and cheap method for the modification of the hydrophilic properties on surfaces [19,20]. The polymer biocompatibility allows less macrophage adhesion, especially when a blood-aqueous barrier breakdown occurs, as in the case of glaucoma or uveitis [21].

The crystalline lens, together with the cornea, are the main components of the optical system of the eye and

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produces a shield effect against UV radiation damage to the human retina. Every year, millions of patients worldwide undergo cataract surgery with the removal of the opaque lens and IOL implantation in the lens capsule [5] used to correct different refractive errors [22,23]. The IOL represents the main barrier to UV radiation over the life of the implant. Heating or irradiation by UV light enables modifying the curvature radius of the IOL surface, causing aging and deterioration effects on the optical and mechanical properties of the lens [24]. The aging of the polymers due to exposure to UV sources, such as tanning lamps, laser, and ionizing radiations [25,26], may produce a rapid reduction of the optical transmittance inducing, sometimes, the generation of microcracks, yellowing, hardening, and other defects in the transparent medium [27] and potentially impact optical measurements. In particular, IOL transparency can be affected by polymer degradation. In fact, UV radiation at 365 nm wavelength, carrying photons at 3.4 eV, may cause ionizations, radical formation, chain scissions, chemical bond breaking, and multiple photon absorption, generating a strong modification of the irradiated surface layers as a function of the irradiation time. This effect overall changes the composition and the chemical and physical properties of the irradiated layers, leading to a decrease in its optical transparency, according to the literature [28].

UV irradiation is a potential concern for the long-term performance of hydrophilic acrylic IOLs. It can cause a decrease in transparency, polymer yellowing, and potentially alter the optical properties, affecting vision and requiring lens replacement. The extent of the damage depends on the intensity and duration of UV exposure.

Changes in the material properties due to UV irradiation can affect how the IOL interacts with light. This can lead to inaccuracies in optical measurements. A modification of the refractive index, which determines how light bends as it passes through the IOL, can alter the refractive index and the light scattering, affecting the focusing power of the lens. Additionally, UV exposure can decrease the overall light transmission through the IOL.

The IOL absorption of UV light in the range from 280 to 400 nm provides important protection for the retina [29]. Several studies have demonstrated that UV radiation on the retina with a non-UV-absorbing IOL produces retina damage [29]. In fact, UV radiation can trigger the formation of thymine dimers within human dermal melanocytes. Such risk is potentially extended to human retinal melanocytes, especially in cases like the aphakic eye, if the radiation penetrates the inner layers of the eye to reach the retina tissue. The UV-A radiation (λ = 315–400 nm) exhibits a higher efficacy than ionizing radiation, inducing DNA-to-protein cross-links and single-strand breaks in cultured human cells. However, the cornea partially blocks UV transmission, even in an aphakic eye, preventing entirely unhindered UV passage. The crystalline lens absorbs more than 99% of UV radiation in the 300–400 nm range. When exposed to 365 nm UV light, pHEMA may suffer damage to the more superficial layers, with scissions, radical formation, and polymerization reactions, leading to a photo-induced concentration gradient, which has the potential to modify the refractive index of the IOL. UV transmission can be completely blocked by the addition or chemical bonding of chromophores to the IOL material [30]. In this work, pHEMA IOLs have been characterized for their usefulness by attenuated total reflectance coupled to Fourier transform infrared (ATR-FTIR) spectroscopy and by UV-VIS optical spectroscopic analyses after their exposition to a UV source at different exposition times. The goal is to establish IOL aging from exposure to UV radiation at 365 nm and study the damage suffered by the pHEMA molecular structure.

2 Materials and methods

The synthetic hydrophilic acrylic polymer pHEMA is based on pHEMA with peculiar characteristics. The different properties of this polymer depend on the amount of molecular groups methylmethacrylate, hydroxyethyl methacrylate, azobisisobutrylonitrile, and tetrahydrofuran used for its synthesis. The pHEMA polymer has high flexibility with Young's modulus of 50 kPa and high transmissivity in the visible region, with maximum transmittance (84%) reached with the specimen containing 13.26% MMA. It has a glassy transition temperature T_g of about 85°C and a melting temperature of about 68°C. Its water content is 36–44% [31], and its refraction indices at 37°C are 1.52, 1.51, and 1.48 at wavelengths 405, 532, and 670 nm, respectively [32]. The exposure to UV radiation was performed according to ASTM G154 standard [33], employing a UV Blak-Ray lamp UVL-56 [34], centered at 365 nm, corresponding to a photon energy of 3.38 eV. The lamp had a 6 W power, and the fluence was about 200 mJ/cm^2 at about 3 cm from its surface. The presented data reflect the average values of five analyzed IOL samples irradiated in air at room temperature (20°C), 1 atm pressure, and at a humidity rate of 50%. Samples were exposed at a distance of about 3 cm from the lamp at various exposure times on the convex face. The sample employed was an IOLTECH® by Carl Zeiss Meditec® biconvex Intraocular Lens [35], having a diameter of 5 mm and a central maximum thickness of 1 mm, which was estimated using a caliber. The UV penetration depth in the pHEMA is about

100 µm. The changes to the chemical structure (bond scission/forming) of the copolymer after UV irradiation were monitored by ATR-FTIR spectroscopy. A micrograph and a picture of the investigated lens are shown in Figure 1(a) and (b), respectively.

IOLs were irradiated for up to 19 h using a UV lamp in the emission range between 355 and 385 nm wavelength. The maximum exposure time of 19 h came from an approximate calculation we made for the exposure to UV light (from the sun) of an average adult not wearing lenses for an exposure time of about 1 month, as reported in our previous work [22]. The effects of the UV radiation on the IOL were investigated using an FT-IR spectrometer, Jasco 4600, for the ATR coupled to Fourier transform spectroscopy to investigate the chemical changes in the sample before and after UV irradiation at different exposure times. The ATR–FTIR spectra were collected in the wavenumber range from 4,000 to 400 cm^{-1}. All measurements were performed by exerting the same pressure on the lens and the aperture to the diamond crystal. The crystal used for the ATR measurements is a diamond tip.

Reflectance optical measurements were performed employing an AvaSpec-2048 spectrophotometer with UB-600 lines/mm grating and a bandwidth of 195–757 nm. The source was an Avantes deuterium/halogen lamp AvaLight-DH-S with an integrated TTL shutter.

The optical measurements related to the transmittance in the UV-Vis-IR region as a function of the irradiation were performed employing three types of lamps: a UV lamp, with an emission peak centered at 365 nm, a deuterium lamp emitting in a range of 190–400 nm, and a halogen lamp, emitting in the near UV region, between 360 and 2,500 nm.

The changes undergone by UV irradiation were measured through transmittance variations by FTIR and transmission measurements using the Lambert–Beer law. The chemical–physical changes undergone by the acrylic IOLs were also studied by performing wettability measurements.

Optical microscopy was employed for morphology investigation. All UV irradiations were performed at the same experimental conditions (distance lamp – IOL of 3 cm, room temperature [22°C], 1 atm pressure, and 50% humidity rate).

3 Results and discussion

The optical spectra comparison depicted in Figure 2 allows us to observe that the IOL absorbs 365 nm UV radiation. The UV lamp spectrum (black line), acquired by the Avantes spectrometer through a 300 µm diameter fiber, shows a 365 nm centered peak, with an FWHM (full-width at half-maximum) of about 17.5 nm and the maximum intensity normalized to 10^4 counts. Inserting the IOL centrally into the optic path UV lamp spectrometer, using two UV optical fibers, the spectrum is modified. Indeed, the IOL shows a significant reduction of the initial I_0 UV transmitted radiation (I, red line), decreasing the peak at 356 nm to about 7,300 counts, *i.e.*, producing a transmittance of only 73%. This means that the pHEMA has a significant absorption coefficient at this wavelength. Because the pHEMA IOL has a central thickness of $\Delta x = 1$ mm, the absorption coefficient μ of the lens to the 365 nm wavelength is

$$\mu\ (365\ \text{nm}) = \frac{1}{\Delta x}\ln\frac{I_0}{I} = \frac{1}{1\ \text{mm}}\ln\frac{10^4}{7{,}300} = 3.15\ \text{cm}^{-1}. \qquad (1)$$

Figure 3 shows the optical measurements for the IOL illuminated using a UV lamp and increasing the exposure times (at 4.5 and 19 h) and its comparison with the transmission from the untreated pristine polymer and with the lamp emission spectrum (Figure 3a). The reported

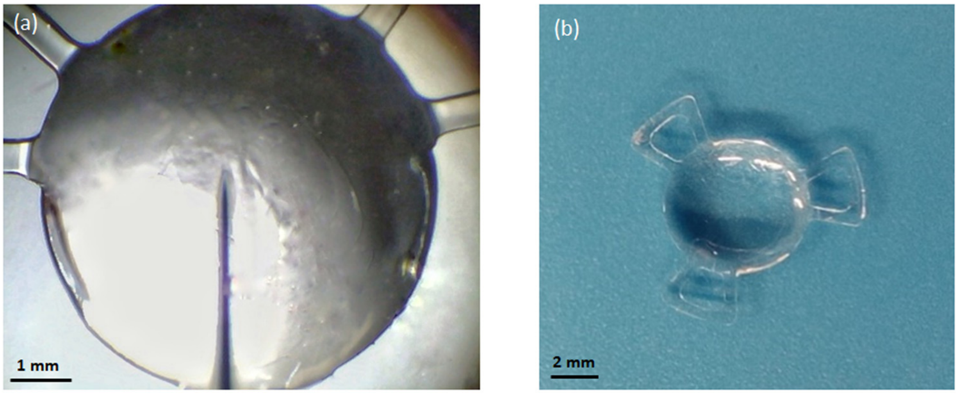

Figure 1: (a) Micrograph and (b) picture of the pHEMA investigated IOL.

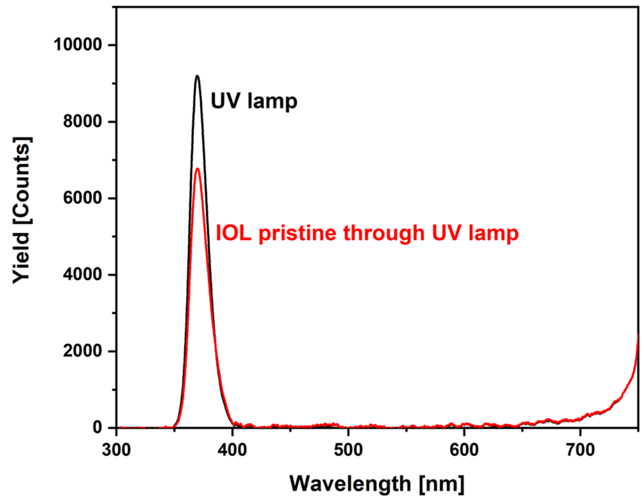

Figure 2: Optical transmission measurements for the IOL illuminated by a UV lamp centered at 365 nm.

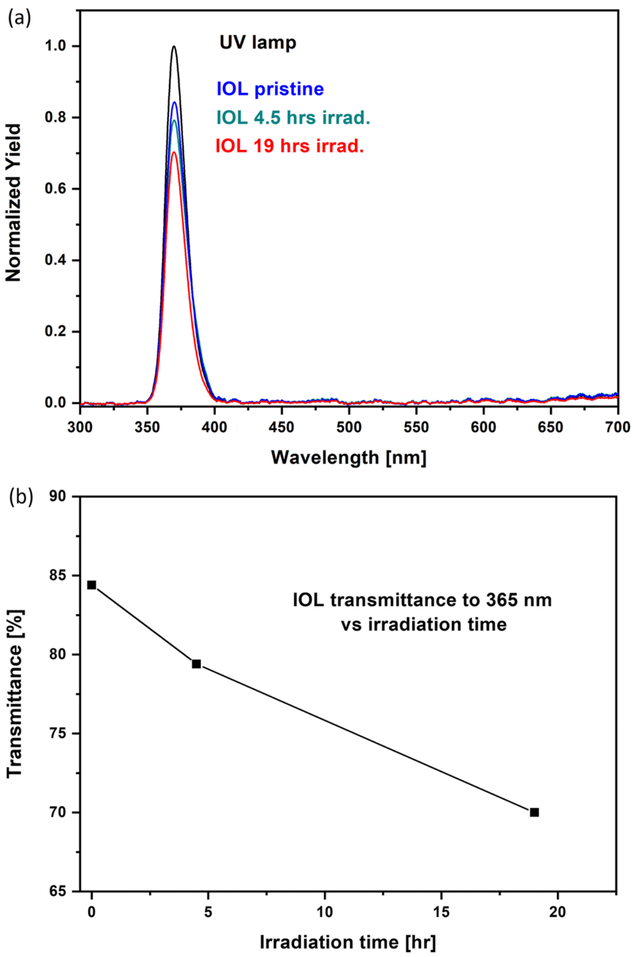

Figure 3: Transmittance spectra *versus* the wavelength for different UV irradiations (a) and transmittance decreasing with the UV irradiation time (b).

transmittance variation *vs* the irradiation time at 365 nm UV irradiation indicates a reduction in the transmittance from 85% up to about 70% after 19 h, *i.e.*, of about 18% with respect to the pristine lens (Figure 3b).

At high UV exposure times in the air, a macroscopic modification of the investigated lens was observed, which significantly changed its softness and elasticity, becoming increasingly harder and less elastic, *i.e.*, acquiring a glassy appearance and optical yellowing. This effect resulted in a slight reduction in the optical transmission of the lens. Figure 4 shows the comparison of the optical measurements for IOL transmission illuminated by the deuterium lamp for the maximum UV irradiation time of 19 h with

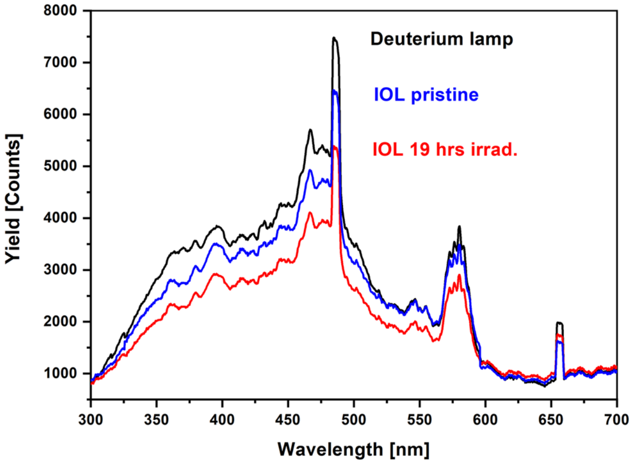

Figure 4: Deuterium lamp emission spectrum and its transmission through the pristine IOL, and comparison with the IOLs treated at 4.5 and 19 h.

that relative to the untreated pristine lens and the lamp emission spectrum (Figure 4a). It is possible to observe a constant decrease of the transmittance in the visible region and a minimum transmittance variation in the UV and IR regions, which is physically shown due to a vitrification of the IOL surface.

The deuterium lamp emitting from the near UV to the visible and to the near IR wavelength ranges allows for the evaluation of the IOL transmission in a wide region, from 300 nm up to about 700 nm, as a function of the UV treatment at the initial phase (*i.e.*, without UV exposure) and at the UV exposure times of 4.5 and 19 h. The measurements shown in Figure 5 demonstrate that the IOL transmittance decreases from the UV region up to the visible region, where it remains about constant for a wide wavelength range, restarting to increase in the IR region. The IOL transmittance at 300 nm decreases from about 95% up to about 90% in the case of maximum UV exposition time (19 h) in the visible region (400–550 nm), and it is about 84% in the case of pristine IOL and reduces to about 70% in the case of the maximum UV exposition time. At long wavelengths, the transmittance increases to 100% in pristine IOL and long-time irradiated lenses. Thus, the higher transmittance reduction in the visible region, at about 500 nm wavelength, is about 18%.

The presented results are also confirmed by the halogen lamp irradiation emitting in the visible and IR regions. The IOL transmission spectra to the halogen lamp are shown for comparison in Figure 6, relative to the pristine IOL, to that irradiated 19 h, and to the lamp emission (normalized to 1,000 counts). In this wavelength region, the transmittance reduction due to the 19 h UV exposition is nearly negligible.

ATR-FTIR spectroscopy allowed us to investigate the different carbon groups and oxygen functional groups present in the IOL before and after UV irradiation at different exposition times. Figure 7 shows the FTIR spectrum of the pristine pHEMA-IOL in the wavenumber range of 4,000–400 cm^{-1}. All the measurements were performed by applying the same pressure on the lens and the aperture to the diamond crystal. The band between 3,380 and 3,401 cm^{-1} is assigned to ν(O–H), the stretching vibration of pHEMA [36]. The band in the region 2,930–2,950 cm^{-1} corresponds to the stretching vibrations of ν(CH_3), according to the literature [37]. It also manifests the CO_2-absorbed gas at around 2,340 cm^{-1} [22]. The strong peak at 1,709 cm^{-1} is assigned to the C═O bonds, while the peaks at 1,644 cm^{-1} and 1,156 cm^{-1} can be attributed to N–H bending and C–O bonds, respectively [38,39].

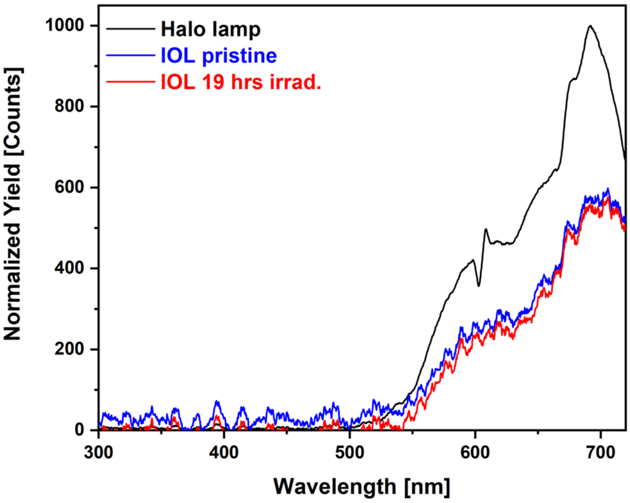

Figure 6: Spectra comparison relative to the halogen lamp and its transmission in IOL pristine and 19 h UV irradiation.

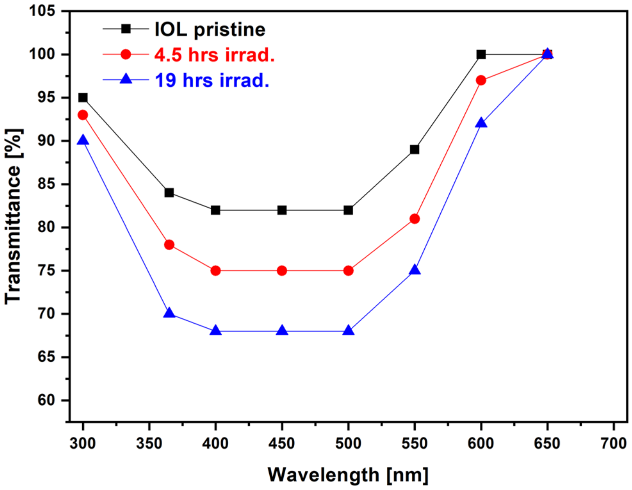

Figure 5: IOL transmittance in UV, visible, and IR regions for pristine and irradiated regions.

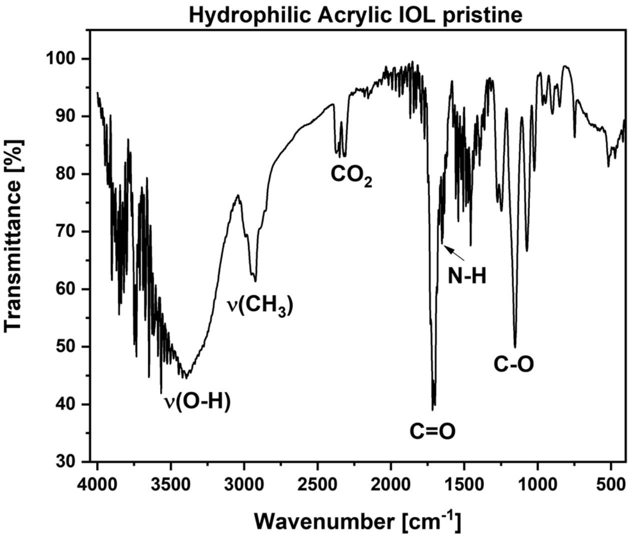

Figure 7: ATR-FTIR spectrum of the pristine pHEMA-IOL.

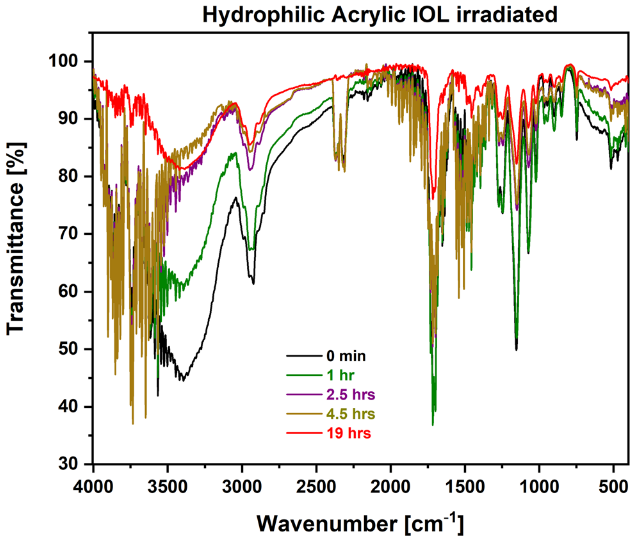

Figure 8: FTIR transmittance *versus* the wavenumber in the IOL for different UV irradiation times.

The average transmittance at low wavenumbers is about 90%, while it decreases to about 70–80% at higher wavenumbers, where the ν(O–H) absorption bands are present. After UV irradiation, especially increasing the exposure time, the intensity of almost all the observed peaks was found to be reduced. These changes in the FTIR spectra may be because of the chemical bond breaking, radical formation, scissions, and cross-links generated by its energy deposition. Figure 8 shows the comparison of the spectra for different irradiation times in air of the pHEMA lens.

A comparison of the spectra shows that as an effect of the UV irradiation time, the FTIR average transmittance increases. Its increment is more incisive in the high wavenumber region (4,000–2,500 cm^{-1}) and less enhanced in the low wavenumber range (2,000–50 cm^{-1}). At about 3,400 cm^{-1}, the transmittance increases from 45% in the pristine lens to about 82% in the long irradiated one, *i.e.*, its increment is about 82%. Moreover, it is particularly evident that the intensity of the strong ν(O–H) groups decreases with the irradiation time, as well as the $\nu(CH_3)$, C═O and C–O groups. This is because UV irradiation breaks the chemical bonds and releases water, oxygen, and hydrogen, thereby reducing the absorption of these groups in the polymer. It is possible to observe that the spectra are heavily contaminated by atmospheric water vapor adsorption, which should compensate for the good legibility of the relevant bands.

Moreover, the detected CO_2 could come from the presence of air between the crystal and the IOL surface. CO_2 gas concentration remains high for low irradiation times, disappearing for long irradiation time in the air, indicating that other mechanisms, such as the production of oxygen radicals and functional groups of oxygen as –OH groups and epoxy groups, may modify its presence in the superficial polymer-irradiated layers. In fact, it is well known that UV radiation ionizes the oxygen molecules in the air and the polymer, producing reactive radicals and oxygen reactive groups, which in turn may generate CO_2 and other compounds. The performed measurements did not use nitrogen leakage.

Further measurements of IOL characterization as a function of the UV irradiation time were performed. One of these concerns is the change in the water-wetting properties of the lens. For each IOL, 20 measurements of contact angle were performed before and after UV irradiation, on different points of the surface, at the experimental conditions of atmospheric pressure, ambient temperature (20°C), and at 50% of ambient humidity.

The measurements were performed by dropping a microliter of distilled water onto the lens surface. The wettability angle was estimated with the aid of an optical microscope.

Figure 9 shows a comparison of an optical microscope photo image between the wetting angle contact measurements in the pristine lens (Figure 9a) and the UV-irradiated lens 19 h (Figure 9b). The measurements demonstrate that

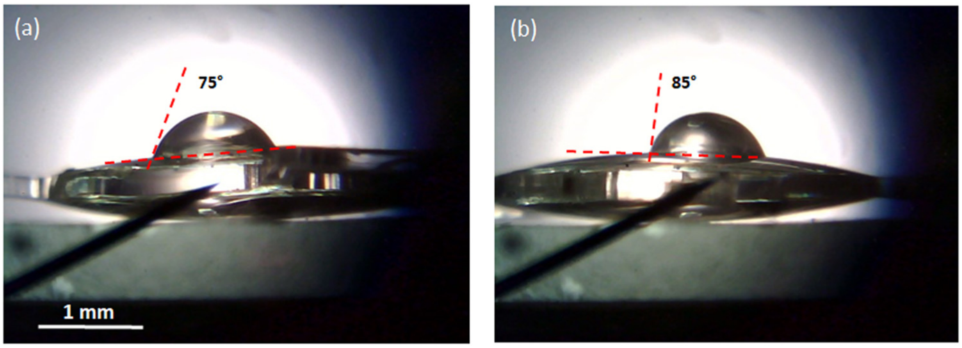

Figure 9: Water contact angle measurements in IOL pristine (a) and UV irradiated for 19 h (b).

the UV irradiation increases the contact angle from 75° in the pristine IOL up to 85° in the long-time-irradiated lens; thus the UV damage decreases the hydrophilicity of the pHEMA surface, which becomes near hydrophobic. These results are in agreement with the literature data [40]. Probably, such modifications also involve the oxygen permeation of the lens. The IOL changes undergone by the UV-irradiated lenses for 19 h highlighted macroscopic changes that, at this stage, have not been quantified. For example, after irradiation, the lens under ambient light appeared less elastic, harder to the touch, and slightly yellowed. The evidence of its possible vitrification could cause a reduction in oxygen permeation. We intend to quantify the variation of these parameters as a function of the irradiation time and as a function of the type of UV lamp used in future work.

4 Conclusions

The aging of pHEMA IOLs has been studied, irradiating the polymer surfaces by a UV lamp emitting at the 365 nm wavelength at different exposure times. The polymer modification, investigated by ATR-FTIR spectroscopy, allowed us to observe that increasing the irradiation time causes molecular breaking and scissions on the hydrophilic/acrylic surface, releasing water, oxygen, and hydrogen, thereby resulting in reduced absorption of the ν(OH), ν (CH_3), C═O, N–H and C–O groups in the polymer. These IOL modifications led to a reduction in the transmittance of the lens in the UV, visible, and IR regions.

The presented work demonstrated that pHEMA IOLs exhibit significant resistance to UV irradiation, retaining their protective qualities even after prolonged UV exposure. However, under long-time irradiation conditions such as 19 h of exposure at high UV intensities, there was a significant reduction in transmittance, particularly in the visible region (at 500 nm), with a decrease of about 18%. This reduction in transmittance in the visible region is critical, as it directly affects the optical performance of the lens. Additionally, the wettability of the lens surface decreased, indicating a shift toward hydrophobicity, which simulates the average UV radiation exposure received by the eye over approximately 1 month without sunglasses.

In contrast, the transmittance in the IR region increased, particularly after 19 h of maximum UV exposure, with an increase of about 82%. This change is attributed to the reduction in oxygen functional groups in the polymer, leading to different optical behaviors in this wavelength range. The ionization of oxygen molecules by UV irradiation also resulted in the generation of CO_2 and other oxygen compounds, further altering the chemical composition of the lens surface.

Wettability measurements demonstrated that prolonged UV irradiation increases the contact angle, making the polymer surface more hydrophobic.

This shift toward hydrophobicity, combined with experimental evidence of potential vitrification, hardening, and yellowing of the lens, could lead to a reduction in oxygen permeability, which will be investigated in future work. The presented study offers new insights into the effects of UV exposure on pHEMA IOLs, revealing both the polymer's stability and the conditions under which its optical properties can deteriorate. While the characteristics of pHEMA are already well-known, this research highlights new aspects of how prolonged UV exposure impacts the material's behavior and performance. Future research will focus on evaluating the PCO rates for hydrophilic and hydrophobic materials, investigating the effects of UV irradiation on IOL oxygen permeability, and examining the degradation of the material under far-UV region irradiation.

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