

Ultraviolet radiation of short wavelength (UVC) induced-modifications in optical properties of PADCM. El Ghazaly^{1,2}, A. Sh Aydarous³, Talal A. Al-Thomali¹¹. Department of Physiology, Faculty of Medicine, Taif University, P.O. Box 888, Taif, KSA². Department of Physics, Faculty of Science, PO 44519, Zagazig University, Zagazig, Egypt³. Department of Physics, Faculty of Science, Taif University, P.O. Box 888, Taif, KSAghazaly2000@yahoo.com

Abstract: The induced optical modifications of poly allyl diglycol carbonate (PADC), which used in fabrication of ophthalmologic lenses, exposed separately to ultraviolet radiation with a short wavelength of 254 nm (UVC) for different durations were investigated. Poly allyl diglycol carbonate (PADC) samples were exposed to UVC from a crossliker, thereafter the UV-Vis spectra were measured using dual beam UV-Vis spectrophotometer at room temperature. The UV-Vis spectra show that the poly allyl diglycol carbonate (PADC) subjected to blue shift before a wavelength of 280 nm and red shift after 280 nm, moreover the absorbance is increased at wavelength of 280 nm. Meanwhile for visible spectra including Red, Blue, and Green, there was no significant change upon exposure to UVC. This behavior indicates the suitability to utilize PADC as a successful UVC blocker without change in the visible light transparency. An isosbestic point is observed in the UV-Vis spectra that shifted to shorter wavelength with increasing the exposure time. The direct and indirect band gaps of PADC were determined, it was found that the indirect and direct band gap decrease with the increase of the exposure time. The direct and indirect optical energy band gaps and the number of carbon atoms in a cluster with modified Tauc's equation are correlated with the exposure time to UVC, where the number of carbon atoms in a cluster increases with the decrease in the optical gap energy.

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1. Introduction

Plastic ophthalmologic lenses based on poly allyl diglycol carbonate (PADC) are widely utilized in last decades because of its excellent optical characteristics (Henshaw, 1982). Furthermore, PADC is being utilized in many scientific applications especially as solid state nuclear track detector for ionizing and non-ionizing radiations detection (Nikezic and KN, 2004, and references therein). The main advantages of the ophthalmologic lenses made up of PADC in comparison with inorganic ophthalmologic lenses (glasses) are its impact strength and its low specific weight for example in their use as lenses for spectacles. PADC lenses are superior to inorganic glasses with respect to breaking, and inferior to inorganic glasses lenses with respect to scratch resistance (Lorkowski, 1994).

PADC is a dense three-dimensional network containing polyallyl chains connected by diethylene glycol dicarbonate link. The monomer contains three functional groups; these are: Allyl group (CH₂=CH—CH₂—), ether group (—CH₂—O—CH₂—), and carbonyl group (C=O) which is located in the center of the main chain. The repeating monomer unit of poly allyl diglycol carbonate (PADC) detector is

depicted in Figure 1 ((Durrani and Bull, 1987), (Tse et al., 2006), (Tse, 2006)). As indicated in Figure 1, the presence of two Allyl groups leads not only to polymerization of PADC's monomers but also cross-link with each other which result in a thermoset plastic characterized by being hard, infusible and insoluble in all solvents (Chapiro, 1962).

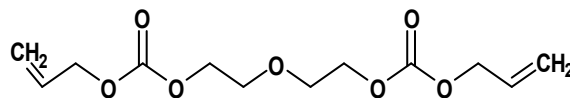


Figure 1. Structure of the PADC monomer unit (Tse et al., 2006).

Exposure of poly allyl diglycol carbonate (PADC) to ultraviolet radiation of short wavelength (UVC) induce chemical modifications through photodegradation, which including crosslinking, chain scission-and aggregation, formation of double bonds and molecular emission ((Dwaikat et al., 2008), (Yu et al., 2003), (El Ghazaly et al, 2012), (Fink and Hnatowicz, 2007), (Wong et al., 1992), (Fink et al. 1995), (Tauc, 1970)). However, the photodegradation give rise to modifications in the optical properties of the poly allyl diglycol carbonate (PADC) which may affect the absorbance of different

wavelengths in the ophthalmologic lenses. The effectiveness of these changes produced in PADC depends on the structure of the polymer as well as the exposure time to UVC ((Fink et al. 1996), (Abu-Jarad et al., 1991), (Abu-Jarad et al., 1997), (Sharma et al., 2005), (Singh et al., 2007)).

Throughout the current paper, the induced modifications in optical properties of PADC upon exposure to UVC with wavelength of 254 nm for different durations will be explored. The correlation between exposure time to UVC and absorbance at different wavelengths will be reported. Moreover, the correlation between the induced modifications in direct and indirect optical band gaps and the exposure time will be investigated. Finally, the number of the number of carbon atoms in a cluster will be determined for direct and indirect transition.

2. Material and Methods

Poly allyl diglycol carbonate (PADC) sheets, TASTRAK type (Track Analysis System Ltd., UK), of density of 1.3 and thickness of 1000 μm were cut in pieces of 4 cm^2 with the aid of a laser beam. PADC samples were exposed to ultraviolet radiation of short wavelength of 254 nm for different durations in air at room temperature. The ultraviolet-cross-linker (Hoefer, UVC 5000 Ultraviolet Crosslinker) was used as UVC source. The UVC 5000 Ultraviolet Crosslinker supplies energy of 102 $\mu\text{J}/\text{cm}^2$. UV-visible spectra were measured, using an UV-visible spectrophotometer (Model Spectro dual split beam, UVS-2700) at room temperature in the wavelength range from 190 to 900 nm keeping air as a reference.

3. Results and Discussion

3.1. Absorption Spectra of PADC

There was no significant change in the physical properties of PADC upon exposure to ultraviolet radiation of wavelength 254 nm. This indicates, however, the relative stability of PADC against UVC. The UV-Vis spectra of pristine and exposed PADC to ultraviolet radiation of 254 nm for different durations are depicted in Figure 2. The absorption in the wavelength is resulting from the presence of chromophores. The strong absorption bands in the region from 190-to-270 nm are resulting from the C=C.

The UV-Vis spectra for UVC-irradiated PADC subjected to blue shift before the wavelength of 280 nm and red shift after the wavelength of 280 nm, which indicates that PADC is subjected to photodegradation upon exposure to UVC. This can be explained by formation of an unsaturated group in a combination with carbonyl group such as α,β unsaturated aldehyde (Tse, 2006). In conjugated

polymers such as PADC, ultraviolet radiation of wavelength 254 nm has sufficient energy of 4.88 eV to cleave some bonds which has bond dissociation energy less than UVC photon energy such as C—C bond (3.5 eV) and H—C bond (4.29 eV). Also UVC interacts with PADC chains through the production of free radicals, which can initiate further reactions with molecular oxygen which results in photo-oxidation. These results in the splitting of the macromolecular chains (Tse et al 2006), this stimulates significant change in UV-Vis spectra of PADC as depicted in Figure 1. For prolong exposure times there are a slightly changes in the UV-Vis spectra showing a saturation effect. There are different shifts are clearly visible on the UV-Vis spectra of PADC exposed to UVC; these are: the blue shift in the UV-Vis spectra before the wavelength 280 nm and red shift in the UV-Vis spectra after the same wavelength. Unfortunately, there is no explanation for such effect although the measurements have been measured many times, the effect has been observed in all samples.

An isosbestic point is observed in the UV-Vis spectra approximately at 280 nm which is nearly constant at shorter exposure times, namely until 4 hours. For prolonged exposure times isosbestic point is shifted to shorter wavelength. The existence of isosbestic point indicates that there are two species in the reaction that are related linearly by stoichiometry; therefore the absorbance is invariant at particular wavelength.

Figure 3 shows the net change in absorbance of PADC upon exposure to different durations. One can recognized that the significant changes occur in the wavelengths range from 220 to 400 nm which represent the ultraviolet region in electromagnetic spectrum. This strong absorption is attributed to the C=C bond, which is associated by $\pi\rightarrow\pi^*$ transition, which happens in unsaturated centers in the molecules contain double bonds (Nikezic and KN, 2004). However, for visible light wavelengths, the absorbance of PADC is nearly constant and is independent of the exposure time to UVC.

The change in the absorbance at different wavelengths is examined to explore the effect of UVC on the absorbance of visible light and UVC in PADC. Figure 4 illustrates the absorbance of PADC at wavelengths 280 nm (UVC), 472 nm (blue), 543 nm (green), and 683 nm (red) as a function of the exposure times. For visible light colors, the average absorbance amounts to (0.053 ± 0.02) . There are no significant modifications in the absorbance of PADC irrespective the exposure time to UVC, which indicate that UVC causes no effect in the absorbance of visible light. However, the absorbance of PADC at 280 increases from 0.042 of pristine PADC to 0.798

at exposure time of 65 hour. In conclusion, the absorbance of PADC increases exponentially as the exposure time increases to UVC and finally getting saturated for prolonged exposure times using the following equations.

$$Abs(t) = a + [1 - a_1 Exp.(-ta_2)] \quad (1)$$

Where $a = -0.15$, $a_1 = 0.48$, $a_2 = 0.038 \text{ hour}^{-1}$ are fitting parameters. The saturation of the absorbance for increased exposure time can be explained by the formation of a superficial cross-linked layer, which prevents the penetration of oxygen, consequently retard the scission rate therefore no longer increase in absorbance to prolonged exposure time to UVC (Tse, 2006). This performance of PADC enhances the protection of PADC from ultraviolet radiation of short and even longer wavelengths.

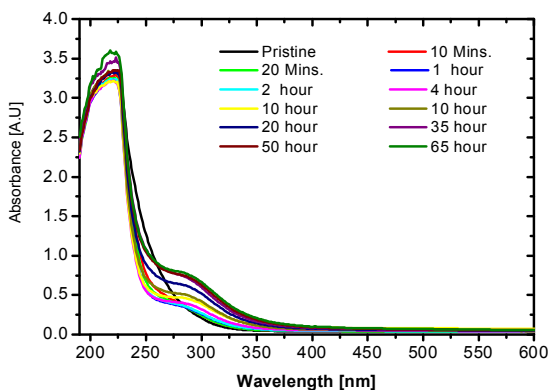


Figure 2. V-Vis spectra of pristine PADC and PADC exposed to UVC with a wavelength 254 nm for different durations at room temperature.

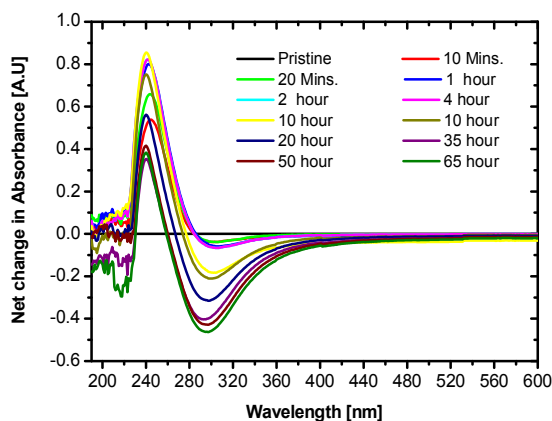


Figure 3. Net change in UV-Vis spectra of pristine PADC and PADC exposed to UVC for different durations.3.2 UV-Vis spectra

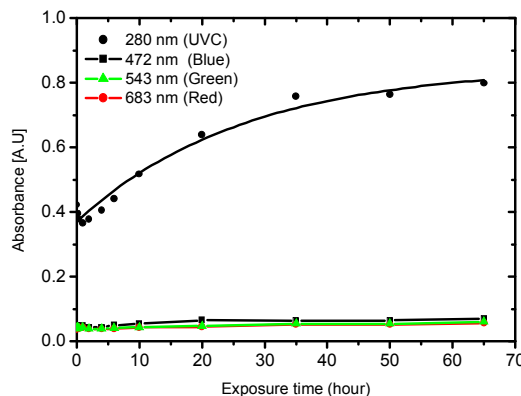


Figure 4. Absorbance of PADC at different wavelengths as a function of exposure time of UVC.

3.2. Optical Band Gaps of PADC

The optical absorption coefficient, α , of PADC reflects its ability to stop and degradation by the incident radiation, it is a crucial element it the response of PADC to UV radiation. In principle, the higher the stopping power, the higher the degradation of PADC. The optical absorption coefficient (α) of PADC depends on the ultraviolet wavelength; it is calculated from the UV-Vis spectra by using the equation (Migahed and Zidan, 2006):

$$\alpha(h\nu) = 2.303 \frac{Abs(h\nu)}{d} \quad (2)$$

where d is thickness in cm and Abs is defined by $Abs = \log(I_0/I)$ where I_0 and I are the intensity of incident and transmitted beams, respectively. The absorption coefficient for non-crystalline material can be expressed as a function of the optical gap energy between the valance-and the conduction band E_g and the photons energy $h\nu$ via the following equation (Tauc, 1970):

$$\alpha(h\nu) = \frac{C(h\nu - E_g)^n}{h\nu} \quad (3)$$

where n is the power, which characterizes the transition process in the K-space. It can assume the values 0.5, 1.5, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden, respectively (Tauc, 1970). The indirect and direct band gap energies are determined by plotting $(\alpha h\nu)^{0.5}$ as shown in Figure. 4 and $(\alpha h\nu)^2$ against the photon energy ($h\nu$) as shown in Figure 5. By considering the linear section of the fundamental absorption edge of the UV-Vis spectra and find the intercept of the best fit lines on the ($h\nu$) axis. The values of the indirect

and direct band gaps energies are represented in Figure 7.

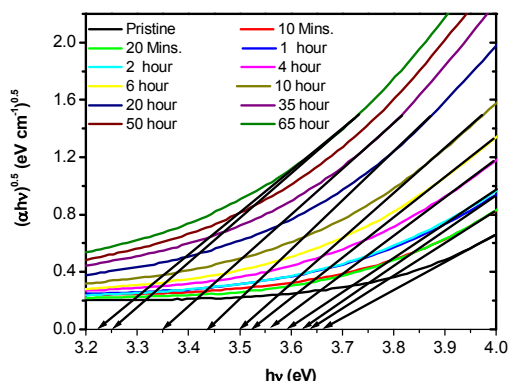


Figure 5. Plot of $(\alpha hv)^{0.5}$ versus photon energy ($h\nu$) in CR-39 polymer before and after exposure to ultraviolet radiation of wavelength 254 nm.

One may observe two important features from Figure 7; the first one is both direct and indirect band gap energy is decreasing with the increase in the exposure time, the second one the indirect band gap is lower than the corresponding values for the direct band gap energies (Fink et al., 1996).

The represented results show some disagreement with the results reported by Tse (2006), which could be attributed to utilizing of a different type of PADC polymer, which are prepared in different ways (e.g., different initiator, different inhibitors, the polarization process, etc.).

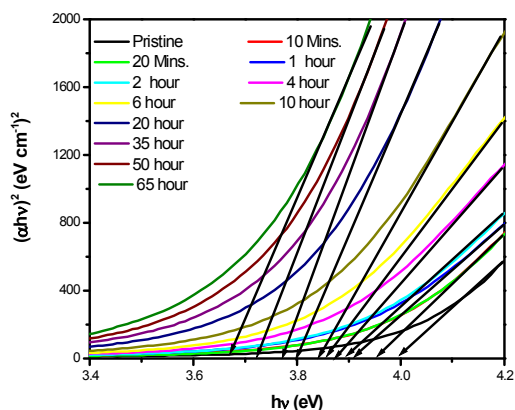


Figure 6. Plot of $(\alpha hv)^2$ versus photon energy ($h\nu$) in CR-39 polymer before and after exposure to ultraviolet radiation of wavelength 254 nm.

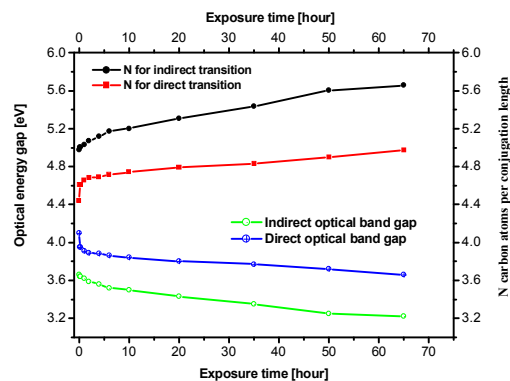


Figure 7. Direct and indirect optical band gaps as a function of exposure time of UVC of 254 nm.

Figure 6. shows the dependence of direct and indirect optical band gaps as a function of exposure time of UVC of 254 nm. Several characteristic points concerning the indirect band gaps deduced from Figure 6. can be noted: (1) the values of indirect band gap is less than the corresponding values of direct band gap of PADC; and (2) The values indirect and direct band gaps decreases by the increase of exposure time to UVC. Such a decrease in E_g of PADC can be attributed to the formation of new photochemicals, which form the trap levels between the HOMO and LUMO energy states, making the lower energy transitions feasible and results in the reduction of the optical band gap.

The value of the optical energy gaps are correlated with the number, type, structural arrangement of the carbon bonds per linear string, the case for PADC. In PADC, which is characterized by linear chain structure, the red shift of the absorption edge upon UVC irradiation is attributed to the increase in conjugation length (Tes, 2006). The number N of carbon atoms per conjugation length is given by (Singh et al., 2007);

$$N = \frac{2\beta\pi}{E_g} \quad (4)$$

Where β is the band structure energy of a pair of adjacent π sites (C=C bond), where β is equal to -2.9 eV and it fits well for the $\pi \rightarrow \pi^*$ optical transition. The indirect and direct carbon atoms as a function of the exposure time to UVC are depicted in Figure 6. One can recognize that The number of carbon atoms per conjugated length is decreasing with increasing the exposure time to UVC, for example it decrease from 4.2 eV for a pristine PADC to 3.2 eV for exposure time of 65 hour.

CONCLUSIONS

Ploy allyl diglycol carbonate (PADC) shows substantial modifications in its optical properties upon exposure to ultraviolet radiation of short wavelength (UVC) of 254 nm. While the absorbance of PADC increases significantly in the wavelength range from 220 to 400 nm, for visible light wavelengths, the absorbance of PADC is nearly constant and is independent of the exposure time to UVC. Direct and indirect optical energy band gaps and the number of carbon atoms in a cluster with modified Tauc's equation are correlated with the exposure time to UVC. In conclusion, PADC can be used successfully as a protector from UVC.

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Corresponding Author:

Dr. M. El Ghazaly

Department of Physiology

Faculty of Medicine, Taif University

P.O. Box 888, Taif, KSA

E-mail: ghazaly2000@yahoo.com

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