

## Thermal annealing induced alterations of optical properties in a CR-39 polymeric nuclear track detector

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**ABSTRACT:** Isochronal annealing experiment was conducted on poly allyl diglycol carbonate (PADC) commercially known as a CR-39 detector. The detector films were subjected to thermal treatment at 130, 140, 150 and 160 °C for annealing time of 8 h. The qualitative impacts of these treatments have been analyzed by means of ultraviolet/visible (UV/Vis) spectrophotometry in the range 190–800 nm, considering optical properties such as absorbance, band-gap energy, and Urbach energy. As control, CR-39 detector film non-subjected to thermal treatment (pristine film) was also examined. This paper shows how the well-controlled thermal treatment of the PADC detector can alter its optical properties in the near-surface layer of thickness beyond a couple of hundreds of nanometers. This finding is more pronounced for cases of higher annealing temperatures and larger annealing time intervals. The measured absorbance, direct and in-direct band gaps, Urbach energy and carbon atoms per conjugated length were proved to be highly affected by increasing the thermal annealing temperature ranging from 130 to 160 °C for 8 h annealing period of time.

**KEYWORDS:** PADC; CR-39 detectors; Thermal annealing; optical properties; band gap energy; Urbach energy; carbon atoms per conjugated length..

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### I. INTRODUCTION

Poly allyl diglycol carbonate (PADC), also known as Columbia Resin 39 (CR-39) plastic, is widely used as a solid-state nuclear track detector (SSNTD) and was first introduced by Refs. (B.G. Cartwright et al, 1978) (R.M. Cassou, 1978). On a microscopic level, temperature is linked to molecular mobility in a physical system like PADC. When polymers, PADC film is a partly crystalline polymer with a dominant amorphous phase (A.F. Saad, 2023), are heated in their solid state, they decompose due to changes in chain mobility. Molecular movements are activated above a particular annealing temperature, and the polymers become more elastic. Changing the degree of chain-secession in the polymer, followed by crosslinking, will fix the iso thermal phase transition temperature (A.F. Saad, 2023).

Some research groups have already investigated the effects of thermal annealing on PADC material (A.F. Saad et al, 2012) (M.A. Rana, 2019) (V. Kumar et al, 2011). Finally, the goal of this work is to use a UV/Vis spectrophotometer to investigate the effects of varied durations of heat annealing on a CR-39 polymeric detector material. A technique for observing detector-film thermal degradation is proposed by integrating all of these thermal-dose-dependent variations in optical characteristics (i.e., absorbance, Urbach energy, optical band gap energy: direct and indirect, and number of carbon atoms per conjugated length).

### II. EXPERIMENTAL PROCEDURE

Track Analysis Systems Ltd. (TASL), Bristol, UK, supplied the PADC detector sheets of TASTRAK with a thickness of 750 µm for the current investigation. For this experiment, four samples of PADC detectors were prepared and annealed in a temperature-controlled oven for 8 h time intervals at varied temperatures, along with a non-thermally treated sample (pristine sample) for control. UV-VIS spectroscopic analysis was performed on these samples. The optical changes caused by thermal annealing at various annealing temperatures for 8 hours

were investigated using various experimental instruments. The detector films were all treated by identical thermal annealing conditions for varied temperatures in a digitally controlled oven. The oven, which can work in temperatures ranging from 5 °C above ambient to 300 °C, was made by the German company Binder Co. (Model: FP 720). The UV-Visible spectrophotometer Model (Spectro UV-Vis 2800, USA) was used with a scanning speed of 25 nm/min in Abs. spectrum mode (ABS mode). The spectrometer's operational wavelength range is 190–800 nm. The instrument has a variable spectral bandwidth of 5, 2, 1, and 0.5 nm in the UV/VIS region, with a wavelength precision of 0.30 nm.

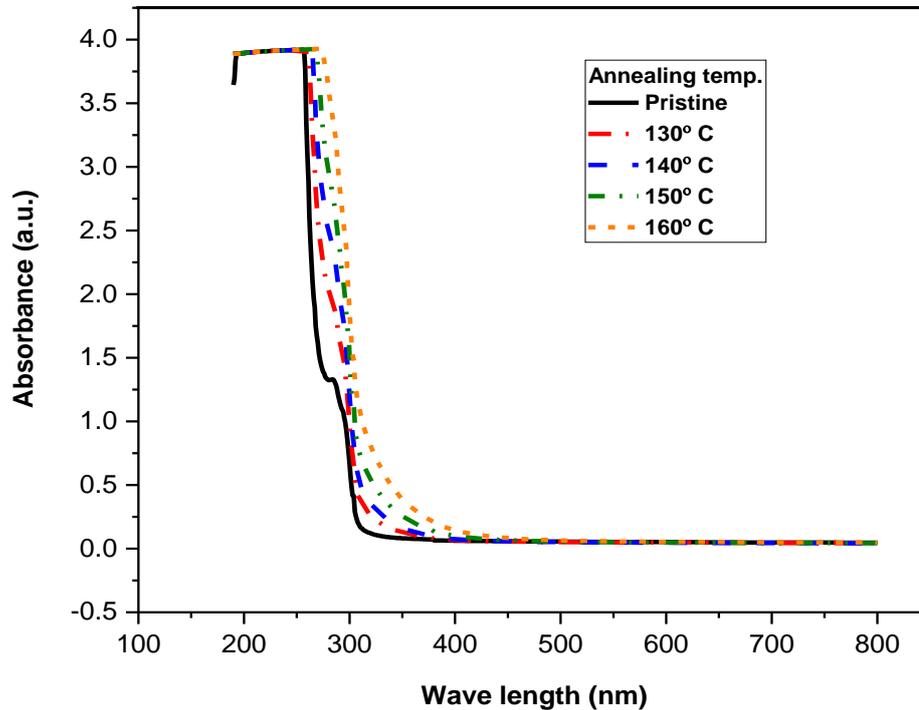
### III. RESULTS

#### 3.1 Measurement of optical absorbance through thermally treated PADC films

The virgin and annealed PADC samples underwent UV-Visible spectroscopy in the wavelength range of 200–800 nm at room temperature. The UV-Visible absorption spectra of virgin and PADC films subjected to heat annealing are displayed in Fig. 1 as a typical illustration. In this figure, the optical absorbance of thermally treated PADC films is examined after being thermally annealed for 8 hours at four distinct temperatures: 130, 140, 150, and 160 °C. As can be seen in Fig. 1, the optical spectra of annealed PADC films exhibit an improvement and a shift of the absorption edge towards longer wavelengths with increasing annealing temperature. As can be seen most clearly in Figure 1, these observed variations in optical spectra are caused by systematic thermal annealing effects rather than random statistical variations. The internal shape of the polymer is altered by heat, as has previously been shown, according to UV-Visible absorption spectra of PADC polymeric material heated between 130 and 160 °C (A. Aframian, 1978). The average random translational kinetic energy of the molecules may be responsible for the probable rearrangement of the polymer chain spacing, according to these experimental findings. As a result, the registration properties of the ionizing particles, for example  $\alpha$ -particles as a heavy ion with low ionization rate and fission fragments as a heavy ion with high ionization rate are altering as a result of this thermal annealing process (A.F. Saad et al, 2021). The mechanisms that result in changes in the track etch parameters as a result of heat treatment have also been noticed by other researchers and us in the past (C.F. Wong, 1984) (A.A. Abou elkhier et al, 1995) (N.E. Ipe, 1986) (M.A. Rana, 2019) (A.F. Saad et al, 2014) (R.K. Jain et al, 2012). The development of thermal annealing-induced flaws is responsible for the broadening of the peaks. These flaws may cause the emergence of new energy levels, which would widen the peaks.

**Table (1): optical band gap energy, photon energy, urbach energy, and carbon atoms (N) in a cluster of PADC polymer-based NTDs exposed to thermal pulses.**

Annealing temperature (°C)	Band gap energy		Phonon energy (eV)	Urbach energy (eV)	Carbon atoms (N) per conjugated length	
	Direct	Indirect			Direct	Indirect
Pristine	4.57 ± 0.03	3.84 ± 0.01	0.73	0.27	3.99 ≈ 4	4.75 ≈ 5
130	4.44 ± 0.01	3.76 ± 0.02	0.68	0.31	4.10 ≈ 4	4.85 ≈ 5
140	4.33 ± 0.02	3.69 ± 0.01	0.64	0.32	4.21 ≈ 4	4.94 ≈ 5
150	4.16 ± 0.04	3.15 ± 0.03	1.01	0.49	4.38 ≈ 4	5.79 ≈ 6
160	3.97 ± 0.01	2.95 ± 0.02	1.02	0.41	4.59 ≈ 5	6.18 ≈ 6



**Fig. 1. UV-visible spectra of the pristine and thermally treated PADC films at different annealing temperatures 130, 140, 150 and 160 °C for a duration of 8 h.**

### 3.2 The Urbach energy

The absorption coefficient can be calculated from the absorbance by using the following formula (M. Fox, 1987)

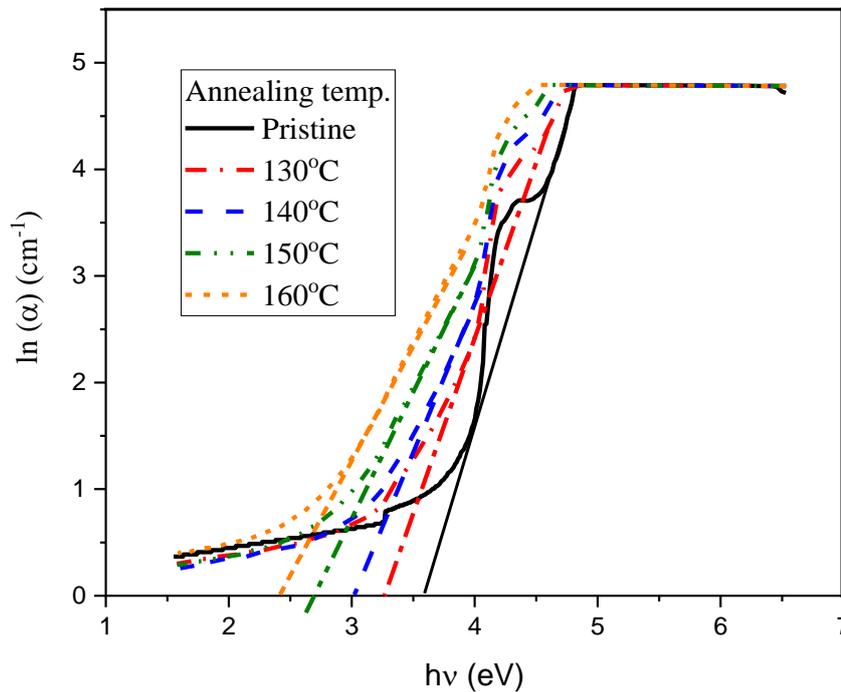
$$\alpha(h\nu) = A/\ell \quad (1)$$

where,  $\ell$  is the sample thickness in cm and  $A$  is defined as  $I_0 - I_t$ , where  $I_0$  and  $I_t$  are the intensity of the incident and transmitted UV-VIS beams, respectively. The absorption coefficient is very small below the band edge in insulators and follows the Urbach relation (F. Urbach, 1953),

$$\alpha(h\nu) = \alpha_0 \exp(h\nu/E_u) \quad (2)$$

Where,  $\alpha$  is the absorption coefficient, which is a function of photon energy  $h\nu$ ,  $\alpha_0$  is a constant and  $E_u$  is Urbach energy and equal to the inverse logarithmic slope of the absorption coefficient.

Figure 2 presents logarithmic-scale plots of the absorption coefficient  $\alpha$  as a function of the photon energy  $h\nu$  for the pristine and thermally treated CR-39 detectors, at different annealing temperatures ranging from 130 to 160 °C for duration 8 h. The Urbach energy  $E_u$  values are tabulated and listed in Table 1. The results revealed that the values considerably increased as the annealing temperature also increased, which may be attributed to an enhancement of decompose owing to chain scission in the CR-39 detectors as a result of thermal annealing up to a temperature of 160 °C. It is interesting to note that the level of damage sustained increased from 130 to 150 °C. On the contrary, the results are slightly lower in the 160 °C sample. For all temperatures at 8 h, enhanced systematic behavior in the Urbach energy values, which reflected the increase in the degree of disorder, is seen for all three annealed samples except 160 °C, which could be due to degradation occurring in the PADC polymer materials that were thermally annealed. At high temperatures for 8 hours, the components of the PADC polymer's lengthy backbone chain began to break and reacted with other broken changes, altering the polymer's characteristics.



**Fig. 2.** Logarithmic variation of the absorption coefficient  $\alpha(h\nu)$  as a function of the photon energy ( $h\nu$ ), for the pristine and CR-39 exposed to thermal heating with different doses. Thermal annealing was performed at 130, 140, 150 and 160 °C for a duration of 8 h. The solid lines show the best-fitting lines of the linear parts of the curves. The values of the Urbach energy are determined by taking the reciprocal of the slopes of these linear fits.

### 3.3. Optical band gap energy: direct and indirect transitions

The previous equation was modified into a more general form by Davis and Mott (N.F. Mott, 1979):

$$\alpha(h\nu) = B(h\nu - E_g)^n / h\nu \quad (3)$$

Where,  $h\nu$  is the energy of the incident photons, the factor B depends on the transition probability and can be assumed to be constant within the optical frequency range,  $E_g$  is the energy value of the optical band gap between the valence band and the conduction band, and  $n$  is the power that characterizes the electronic transition, regardless of whether it is direct or indirect during the absorption process in K-space. Specifically,  $n$  is 2, 3, 1/2 and 3/2 for the indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. The electron wave vector must clearly change significantly when jumping from the valence band to the bottom of the conduction band if the band gap is indirect. It is not possible to make this jump through absorption of a photon alone; the transition must also involve a phonon to conserve momentum. This contrasts with the process for a direct band gap, in which the process can take place without any phonons being involved. The phonon energy  $\varepsilon$  can be calculated based on the energy difference between the optical band gap energy transitions (direct,  $E_g^d$ , and indirect,  $E_g^{ind}$ ) using the following formula (A.F. Saad et al, 2014):

$$\varepsilon = E_g^d - E_g^{ind} \quad (4)$$

However, indirect absorption is extremely relevant in technologically important materials, such as certain metals and amorphous materials. Because of the function of the phonons, the treatment of indirect absorption is more involved than that of direct absorption (M. Fox, 1987).

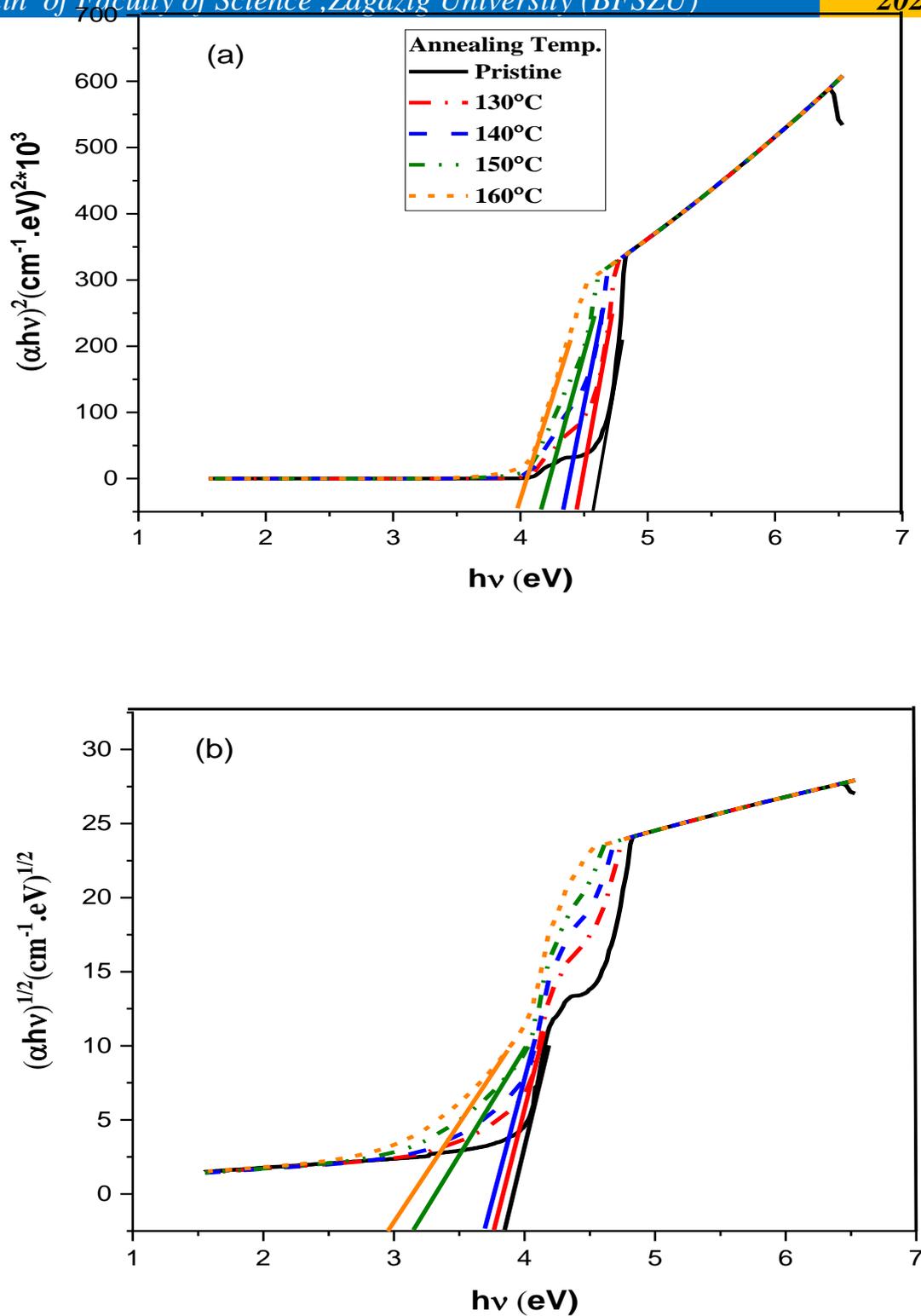


Fig. 3. Plots for optical band gap (eV) in pristine and thermally treated PADC films at different annealing temperatures 130, 140, 150 and 160 °C for a duration of 8 h. The solid linear lines stand for the fitting lines of the straight parts of the curves to the energy axis ( $h\nu$ ). The extrapolation of these solid linear lines to the energy axis ( $h\nu$ ) yields the optical band gaps a) direct and b) indirect.

The optical band gap based on the UV-visible absorption measurements of the non-annealed (pristine sample) and annealed PADC polymer films was calculated by extrapolation of the plot of versus along the axis. The plots between and as well as, respectively, are presented in Fig. 3. The values of extrapolated intercept for four different annealing temperatures as well as the pristine sample are listed in Table 1. Notably, the band gap for the annealed CR-39 detector films subjected to thermal annealing at different temperatures compared the non-thermally treated (pristine sample) decreased from  $3.84 \pm 0.01$  eV to  $3.76 \pm 0.02$ ,  $3.69 \pm 0.01$ ,  $3.15 \pm 0.03$  and  $2.95 \pm 0.02$  eV, and from  $4.57 \pm 0.03$  eV to  $4.44 \pm 0.01$ ,  $4.33 \pm 0.02$ ,  $4.16 \pm 0.04$  and  $3.97 \pm 0.01$  eV corresponding to annealing temperatures of 130, 140, 150 and 160 °C for a duration 8 h for indirect and direct transitions, respectively, as seen in Table 1. The optical changes in comparison to the pristine material are clearly visible as systematic effects at all annealing temperatures, but it may be more unambiguous at higher annealing temperatures, as previously mentioned. The band gap has been seen to gradually decrease with increasing annealing temperature. The formation of unsaturated bonds in thermally treated regions produces more delocalized electrons, which require less energy to enable electronic transitions between different levels. As a result, the absorption edge shifts to longer wavelengths (lower energy areas), resulting in a narrowing of the band gap.

### 3.4 The number of carbon atoms in a cluster

The following formula gives the number of carbon atoms  $N$  per conjugation length for a linear structure known as a cluster (D. Fink et al, 1995):

$$N = 2\beta\pi/E_g \quad (5)$$

where,  $2\beta$  denotes the band structure energy of two adjacent  $\pi$  sites. Because this value is connected with the optical transition in the structure. The value of  $\beta$  is assumed to be -2.9 eV because this value is associated with the optical transition in the structure. The number of carbon atoms per conjugated length remained constant as the thermal annealing temperature increased for the annealed detectors at 130, 140, and 150 °C, including direct transitions. At the highest temperature 160 °C, as shown in Table 1,  $N$  per conjugated length increases to a value of 5 thereafter, as compared to the pristine sample. Notably, in the case of indirect transitions,  $N$  per conjugated length increased to a value of 6 at thermal annealing temperatures of 150 and 160 °C, whereas at lower temperatures of 130 and 140 °C, this  $N$  remained constant as shown in Table 1. As a result of thermal annealing, this phenomenon indicated the creation of extensive systems of conjugate bonds. Furthermore, for the pristine and thermally treated CR-39 polymer detectors subjected to thermal heating at different temperatures, the number of carbon atoms per conjugated length for the indirect band gap energy was comparatively large compared to the direct band gap.

## IV. Conclusion

The analysis of the UV-visible spectra of pristine and annealed PADC film-based NTDs led to the following conclusions: UV-visible spectra detected the existence of a thermal decomposition of the backbone of PADC polymer at annealing temperature 130, 140, 150 and 160°C for a duration period of 8 h, even at the lower annealing temperatures. The obtained results suggest that the extent of heat-induced damage is annealing temperature-dependent. Thermal annealing treatment has proven to be the most efficient process in the current study, which induces continuous steady decreases in the values of optical band gap energy, both of direct and indirect transitions,  $E_d$  and  $E_{ind}$ , respectively, and a modest increase in the values of photon energy  $E_p$ . The decrease in the optical band-gap energy can be mainly attributed to the formation of unsaturated bonds, which give rise to carbon-enriched conjugated lengths in which  $\pi$ - $\pi^*$  transitions of delocalized electrons can occur as a result of thermal annealing. On the other hand, the increase of Urbach's energy can also be ascribed to the increase in the degree of disorder state of that PADC polymer.

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