

Surface effect of ultraviolet radiation on electrochemically etched alpha-particle tracks in PADC

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Abstract

The size of alpha-particle tracks on electrochemically etched ultraviolet-irradiated polyallyldiglycol carbonate (PADC) films were studied. PADC films were first irradiated with 3 MeV alpha particles and then pre-etched chemically using aqueous 6.25 N NaOH solution for 2 h. The films were then exposed to incoherent broad-band ultraviolet (UV) radiation provided by a mercury lamp for different durations up to 2 h. The films were then electrochemically etched in a 6.25 N NaOH solution, with an a.c. voltage of about 1200 V_{eff} and a frequency of 5 kHz, for 2 h at room temperature. The mean sizes of the tracks (or trees) were measured and were found to increase for short UV exposures and decrease for prolonged UV exposures. The results can be explained by the dominance of chain scission at the beginning of UV exposure and the dominance of cross linking for prolonged UV exposure. This explanation is further supported by results from X-ray photo-electron spectroscopy (XPS). Here, the C–O–C bonds decrease for short UV exposures, which is explained by scission of the polymer chains, and increase again for prolonged UV exposure, which indicates cross linking. From nano-indentation measurements, the hardness and the reduced modulus increase monotonically with the UV irradiation. Apparently, these quantities only characterize the amount of cross linking, and do not give information on the initial scission process.

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1. Introduction

It is well established that polymers can be degraded by ultraviolet (UV) radiation (see, e.g., Tse et al., 2006). During UV irradiation of polymers, excited molecules are formed, and then processes such as chain scission and cross linking will take place. The main scission will first cause photo-dissociation and then radical formation. If the free radicals can migrate and recombine with other radicals or the main chain, cross linking will occur. Some of the physico-mechanical properties of the macromolecules are greatly changed by linking them into a network, and the changes are influenced by the degree of cross linking.

Sufficient cross linking can cause bulk gelation in polymers, and thus can be quantified by the sol fraction or the elastic and stress–strain behavior (Herman, 1966). On the other hand,

other techniques are needed if cross linking is limited to the polymer surface. Jaleh et al. (2004) showed that KrF excimer laser irradiation of polycarbonate surface led to skin cross linking, for which Parvin et al. (2005) proposed to use the size of electrochemically etched alpha-particle tracks to characterize.

Polycarbonate is one type of solid-state nuclear track detector (SSNTD). Another one commonly used SSNTD is polyallyldiglycol carbonate (PADC). A recent review on SSNTDs and their applications has been given by Nikezic and Yu (2004). PADC is commercially available under the name CR-39. Recently, Tse et al. (2006) studied the effects of UV radiation on PADC, and suggested that formation of a cross-linked layer could be indicated by the increase of hardness and reduced modulus through nano-indentation. Scission and cross-linking processes were studied in order to explain the change in bulk etch rate of PADC on exposures to UV photons at different wavelengths (Tse et al., 2006).

In the present work, we have used the size of electrochemically etched alpha-particle tracks to characterize the skin cross

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linking in PADC on different exposures to broad-band UV radiation. The results are explained in terms of scission and cross-linking processes. X-ray photo-electron spectroscopy (XPS) as well as nano-indentation measurement results will also be used to characterize the UV-irradiated PADC films.

2. Methodology

2.1. Alpha-particle irradiation, UV exposure, and electrochemical etching (ECE)

For the present work, the PADC films were the CR-39 detectors purchased from Page Mouldings (Pershore) Limited (Worcestershire, England). The PADC films purchased and employed in the present study had a thickness of 100 μm . The PADC films for our study were cut into a size of $2.2 \times 2.2 \text{ cm}^2$.

Alpha particles with an energy of 3 MeV were irradiated under normal incidence on a detector. The alpha-particle source employed in the present study was a planar ^{241}Am source (main alpha energy = 5.49 MeV under vacuum). The energy of the alpha particles was varied by changing the source to detector distance through a collimator under atmospheric pressure. The relationship between the alpha energy and the air distance traveled by an alpha particle with an initial energy of 5.49 MeV from ^{241}Am was obtained by measuring the energies for alpha particles passing different distances through normal air using alpha spectroscopy systems (ORTEC Model 5030) with passivated implanted planar silicon (PIPS) detectors of an area of 300 mm^2 .

After alpha-particle irradiation, the PADC films were pre-etched chemically using aqueous 6.25 N NaOH solution for 2 h. The bulk etch rate for these etching solutions was measured to be about 1.1 $\mu\text{m}/\text{h}$ at 70 °C. The PADC films were then exposed to incoherent broad-band UV radiation provided by a mercury lamp in air at room temperature (from OSRAM) for different durations up to 2 h. The PADC films were then electrochemically etched in a 6.25 N NaOH solution, with an a.c. voltage of about 1200 V_{eff} and a frequency of 5 kHz, for 2 h at room temperature. The images of tracks (or trees) from ECE were captured and the mean sizes of the ECE trees were measured.

2.2. XPS analyses

XPS is a quantitative spectroscopic technique for analyzing the surface chemistry of a material. The studied material is irradiated with X-ray photons while the number and energy of electrons emitted are analyzed. XPS is also known as electron spectroscopy for chemical analysis (ESCA). XPS analyses were performed with an axis ultra-spectrometer (Kratos, UK) by using mono-Al-K α line (1486.71 eV) radiation at a power of 225 W (15 mA, 15 kV) at the Chemical Department in Peking University. To compensate for surface charge effects, binding energies were calibrated by using C 1s hydrocarbon peak at 284.8 eV.

2.3. Nano-indentation measurements

Nano-mechanical properties of PADC films, including hardness and reduced modulus, were measured using a nano-indenter (Hysitron TriboScope with a three-sided pyramidal tips, Berkovich type with 142.3 induced angle). A total of nine indentations were made on each PADC film with an applied load of 5000 μN .

3. Results and discussion

3.1. Electrochemical etching

Typical images of ECE tracks corresponding to different UV irradiation time are shown in Fig. 1. The mean ECE tree diameters were measured and the average ECE tree diameters are shown in Fig. 2. From Fig. 2, we can see that the ECE tree diameter increases for short UV exposures and decreases for prolonged UV exposures.

The results can be explained by the ECE process as well as the scission and cross-linking processes. Tommasino et al. (1980) explained that in ECE, the chemical etchant was forced by the high electric fields to penetrate the insulator around the track tip in a tree-like pattern. This caused degradation of the polymer structure, which was then etched by the reagent.

Tse et al. (2006) studied the effects of UV radiation on PADC and their chemical analyses indicated that both scission and cross linking occurred simultaneously. They suggested that chain scission was a dominant process at the beginning. With chain scission as the dominant process, it would be easier for the chemical etchant to be forced into the PADC film around the track tip, so a larger tree diameter is expected. For prolonged UV exposures, the free radicals created by scission may lead to cross linking to give a branched molecule of a higher molecular weight. As a result, the surface becomes tighter, and it would be more difficult for the chemical etchant to be forced into the PADC film, so smaller tree diameters are expected. This is also the principal behind the proposal of Parvin et al. (2005) to use the size of ECE trees to characterize skin cross linking.

3.2. XPS analyses

The two peaks in the O 1s XPS spectra correspond to (a) the C=O bond and (b) the single bond O in C–O–C. On the other hand, the five peaks in the C 1s spectra correspond to (a) C–C or C–H bonds (C atoms of disconnect), (b) the C–O–C bond (C atoms connecting to 1 O atom), (c) C=O bond, (d)

O–C=O bond and (e) $\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ (C atom connecting to 3 O atoms). The percentages of areas under these peaks in the XPS spectra represent the amounts of corresponding bonds and are summarized in Table 1.

The patterns for the amounts of C–O–C bonds are particularly interesting, which are shown by peak (b) in O 1s and peak (b) in C 1s. The decrease in the amount from 0 to 0.5 h of UV irradiation indicates scission of the C–O bond. Tse et al. (2006)

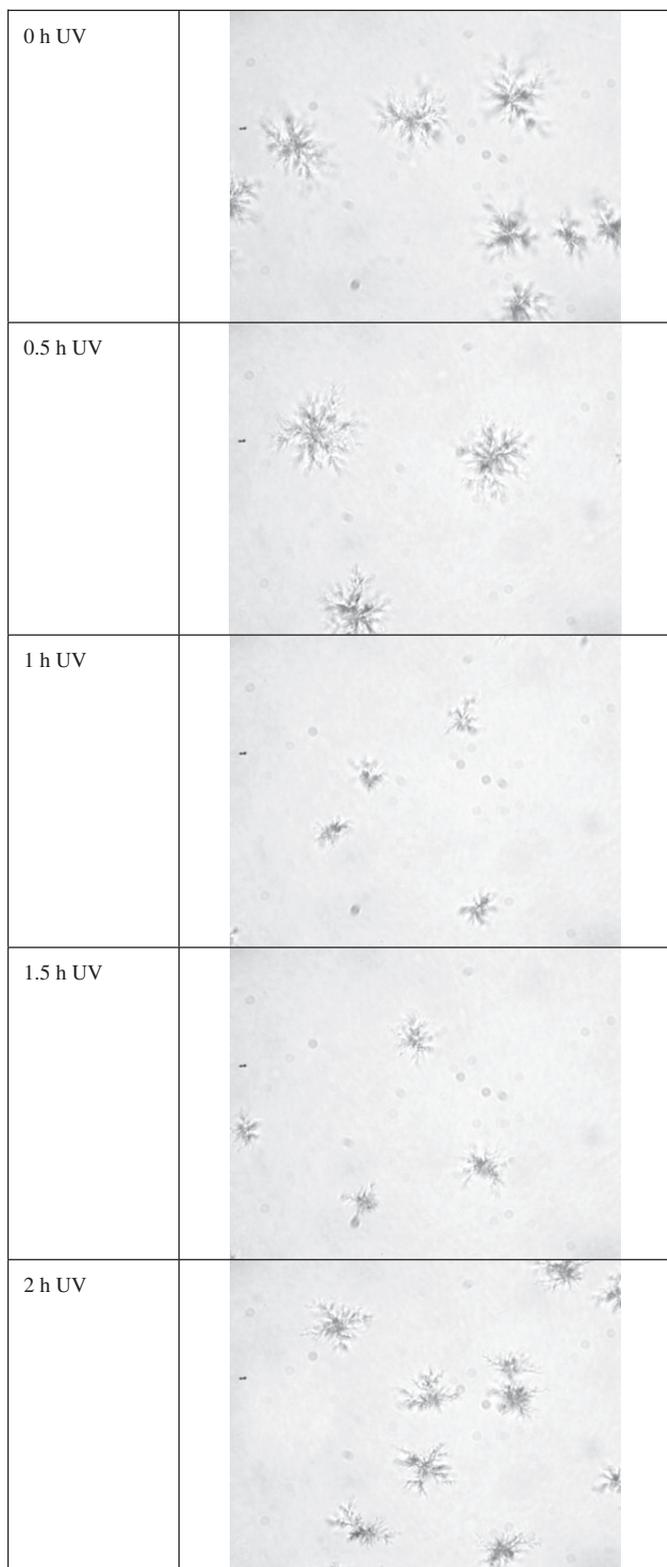


Fig. 1. The image of tracks on electrochemically etched PADc films (in a 6.25 N NaOH solution, with an a.c. voltage of about 1200 V_{eff} and a frequency of 5 kHz, for 2 h at room temperature), which have been irradiated with 3 MeV alpha particles, pre-etched chemically using aqueous 6.25 N NaOH solution for 2 h and exposed to incoherent broad-band UV radiation in air at room temperature for different durations.

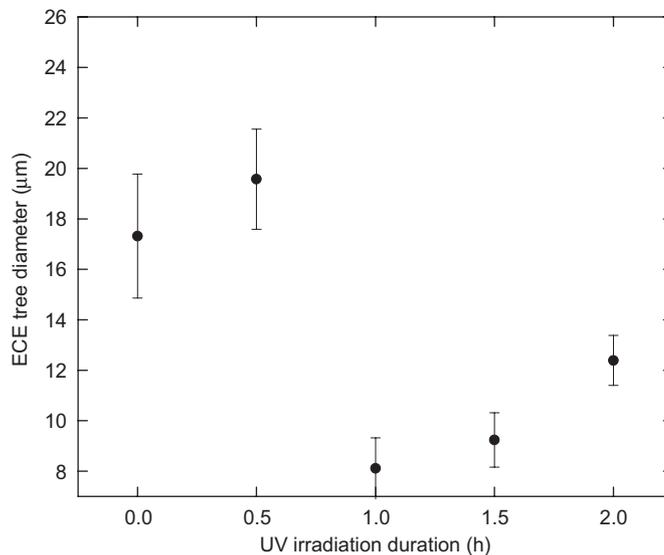


Fig. 2. The average diameters (ECE tree diameters) of the tracks on electrochemically etched PADc films (in a 6.25 N NaOH solution, with an a.c. voltage of about 1200 V_{eff} and a frequency of 5 kHz, for 2 h at room temperature), which have been irradiated with 3 MeV alpha particles, pre-etched chemically using aqueous 6.25 N NaOH solution for 2 h and exposed to incoherent broad-band UV radiation in air at room temperature for different durations.

Table 1

The percentages of areas under the peaks in the XPS spectra for different UV irradiation durations

| Irradiation duration (h) | 0 | 0.5 | 1 | 1.5 | 2 |
|--------------------------|-------|-------|-------|-------|-------|
| O 1s | | | | | |
| (a) | 35.63 | 46.37 | 39.15 | 41.26 | 42.41 |
| (b) | 64.37 | 53.63 | 60.85 | 58.74 | 57.59 |
| C 1s | | | | | |
| (a) | 40.11 | 42.13 | 37.20 | 39.88 | 36.64 |
| (b) | 43.76 | 42.14 | 45.68 | 43.91 | 45.62 |
| (c) | 2.82 | 3.22 | 2.61 | 2.49 | 2.81 |
| (d) | 0.01 | 0.55 | 0.8 | 1.12 | 1.29 |
| (e) | 13.30 | 11.95 | 13.71 | 12.60 | 13.63 |

presented possible mechanisms of photo-oxidation of PADc, which can explain the scission of the polymer chain. At the same time, formation of radicals that contain the $\text{C}=\text{O}$ bond and the $\text{O}-\text{C}=\text{O}$ bond are evident as indicated by the increase in peak (a) in O 1s and peaks (c) and (d) in C 1s.

However, for UV irradiation for 1 h, the $\text{C}-\text{O}-\text{C}$ bond increases abruptly, and its amount for 1 h irradiation and beyond remains at values higher than the value corresponding to 0.5 h of UV irradiation. The increase in the $\text{C}-\text{O}-\text{C}$ bond again indicates that cross linking is taking place. The free radicals generated by UV radiation can combine with different radicals resulting in cross linking (Tse et al., 2006).

3.3. Nano-indentation measurements

The variations of the hardness, reduced modulus, and contact depth of the PADc film measured using a nano-indenter with

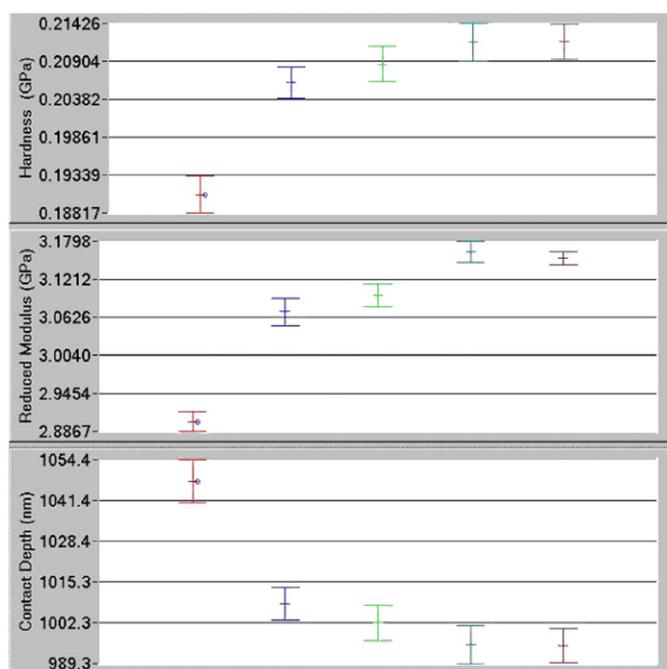


Fig. 3. The variations of the hardness, reduced modulus, and contact depth of the PADC film detectors measured using a nano-indenter with the exposure time to UV radiation. The five data points correspond to (from left to right) UV irradiation time of 0, 0.5, 1, 1.5, and 2 h.

the exposure time to UV radiation are shown in Fig. 3. The five data points correspond to (from left to right) UV irradiation time of 0, 0.5, 1, 1.5, and 2 h. We can see that the hardness and the reduced modulus increase monotonically with the UV irradiation time, while the contact depth decreases monotonically with the UV irradiation time. These patterns are somewhat in contrast to the results for ECE and XPS results shown above. Apparently, the hardness and reduced modulus only characterize the amount of cross linking, and do not give information on the initial scission process. Tse et al. (2006) also determined the nano-mechanical properties of PADC irradiated with UV photons at different wavelengths, and attributed the increased hardness and reduced modulus determined with a nano-indenter to cross linking.

4. Conclusions

- (1) The size of alpha-particle tracks on electrochemically etched ultraviolet-irradiated PADC films were studied. The mean ECE tree diameter increases for short UV exposures and decreases for prolonged UV exposures. The results can be explained by the dominance of chain scission at the beginning of UV exposure and the dominance of cross linking or prolonged UV exposure.
- (2) XPS results were used to support the ECE results. In particular, the C–O–C bonds decrease from 0 to 0.5 h of UV irradiation, which is explained by scission of the polymer chain. However, for UV irradiation time of 1 h and beyond, the C–O–C bonds increase again, which indicates cross linking. The results agree with the ECE results.
- (3) Nano-indentation measurements were also made. The hardness and the reduced modulus increase monotonically with the UV irradiation time. Apparently, the hardness and reduced modulus only characterize the amount of cross linking, and do not give information on the initial scission process.

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