

Photo-degradation of PADC by UV radiation at various wavelengths

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Abstract

The effects of ultraviolet (UV) photons at different wavelengths (namely UVA, UVA + B and UVC) on PADC (polyallyl diglycol carbonate) were investigated in this study. The chemical modifications were studied by Fourier Transform Infrared (FTIR) spectrometry and the corresponding nano-mechanical properties were also determined. The scission process could be revealed by the decreasing net absorbance at particular wavelengths in the infrared (IR) spectra. On the other hand, the cross-linking was indicated by the increased hardness and reduced modulus determined with a nanoindenter. UVA caused no chemical modifications as most of the UV photons in this range were not absorbed by PADC. Both UVA + B and UVC irradiation caused scission of the chemical bonds, which was also manifested by the faster chemical etching rates. The bulk etch rate increased from 1.37 to 5.73 $\mu\text{m}/\text{h}$ for 60 h of UVA + B exposure for 3 h of chemical etching, and increased to 5.13 $\mu\text{m}/\text{h}$ for 60 h of UVC exposure. For 3 h of etching, the bulk etch rate remained unchanged for UVC exposures longer than 20 h. The saturation of the bulk etch rate was due to formation of cross-linked structures on the surface of the PADC samples. It was also observed that a UVC exposure caused a comparatively higher bulk etch rate at the beginning of etching. However, the bulk etch rate decreased with the depth of the PADC sample due to the lower rate of oxygen diffusion into deeper regions.

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1. Introduction

PADC (polyallyl diglycol carbonate), which is commercially available under the name CR-39, is a commonly used solid-state nuclear track detector (SSNTD). CR-39 detectors are widely used in different branches of sciences such as nuclear physics, radon dosimetry and radiobiological experiments. A review on SSNTDs and their applications can be found in Ref. [1].

It is well established that polymers can be degraded by energetic agencies (e.g., ultraviolet radiation) and chemical agencies (e.g., NaOH). There have been many previous studies indicating that ultraviolet (UV) irradiation will affect the bulk etch and track etch responses [2–7]. However, it seems that not all the results in the literature are consistent, and there is limited information on the chemical properties of photo-oxidation. For example, Tidjani [2,3] found that UV exposures

significantly changed the properties, and that the bulk etch rate V_b was increased under broad-band UV exposures. Analyses of Fourier Transform Infrared (FTIR) spectra indicated the increase in hydroxyl group, which was related to the increase in V_b . Abu-Jarad et al. [4,5] suggested that exposures to UVA (at 350 nm) and UVC (at 253.7 nm) caused an increase in V_b , but exposures to UVB (at 300 nm) did not cause an observable variation in V_b . Hussain [6] also identified an enhanced sensitivity (ratio between the track etch velocity V_t and the bulk etch velocity V_b , i.e., V_t/V_b) when CR-39 was exposed to UVA at 360–380 nm. However, Desorbe [7] found no effects on V_b from exposures to UVA at 360–380 nm.

During UV irradiation of polymers, the excited molecules are formed in the first step and then the secondary processes, such as chain scission, cross-linking and oxidation, 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.

In this study, the problem is further investigated through a deeper look at the photo-degradation mechanisms. In

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particular, FTIR spectroscopy was performed to study the photochemical scission of the functional groups, namely C–C, C–H, C–O caused by UV exposure. The formation of a cross-linked layer can be indicated by the increase of hardness and reduced modulus through nanoindentation. Scission and cross-linking processes will be studied in order to explain the change in V_b of PADC on exposures to UV photons at different wavelengths.

The reactions that are involved in the photo-degradation of PADC are largely dependent on the wavelength of the incident UV radiation [8]. The primary objective of this study was to investigate the chemical effect of UV radiation at different wavelengths on PADC. The changes in the properties of PADC under three different UV wavelengths, namely, UVA, UVA + B and UVC will be established in this study. Furthermore, the role of oxygen in the photo-degradation of PADC will also be studied. The varied oxidation rate can result in the variation of V_b with depth [5].

2. Methodology

2.1. PADC films and chemical etching

For the present work, the PADC films were the CR-39 detectors purchased from Page Mouldings (Pershore) Limited (Worcestershire, England). The repeating unit of PADC is shown in Fig. 1. PADC is a highly cross-linked thermoset, which is a dense three-dimensional network consisting of polyallyl chains joined by diethylene glycol dicarbonate link. Two types of PADC films were purchased and employed in the present studies, namely, those with thickness of 1000 and 100 μm . The PADC films with thickness of about 17 μm were prepared by etching the 100 μm PADC films in 0.5 M NaOH/ethanol in our laboratory. The thin 17 μm thick PADC films were irradiated with UV at different wavelengths and the changes in the polymer properties were investigated by FTIR spectroscopy. On the other hand, measurements of the bulk etch rate, hardness and reduced modulus were performed on the 1000 μm thick PADC films. The detectors were etched in 6.25 N aqueous solution of NaOH maintained at 70 $^\circ\text{C}$ by a water bath, which is the most frequently used etching condition for the PADC films.

2.2. UV irradiation

Different UV sources were used to irradiate the PADC films to study the chemical modifications and their corresponding degradation rates. The PADC films were irradiated with UV radiation in air at room temperature. Table 1 shows the wavelengths for the light sources. UVA and UVA + B irradiations

were performed using a xenon lamp (model: XPS 200, from Solar Light Co.), while UVC irradiations were performed using a UVC lamp (model #9815-25, from Cole Palmer).

2.3. FTIR spectroscopy

The FTIR spectroscopy system employed for the present work was the Perkin Elmer Model 16 PC FTIR system. Transmission mode was employed for the present experiments. Some of the absorption bands were identified with the help of a software (Spectrum Search Plus, ver. 2.0, Perkin Elmer). The working wave number range of the spectrometer was from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} . Each PADC film was scanned for 30 cycles to obtain the spectrum, and the absorbance was plotted as a function of the wave number.

2.4. Nano-mechanical properties

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 $^\circ$ 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. Analyses of FTIR spectra of PADC

PADC is a highly cross-linked thermoset fabricated by polymerization of the diethylene glycol bis(allyl carbonate) monomer. It is etched through basic hydrolysis of ester that cuts the carbonate links and liberates the chains in the form of polyallyl alcohol, which is dissolved into the etchant [9].

The significant changes caused by UV irradiation were observed in the whole IR region (4000–400 cm^{-1}) [10]. The absorption peaks corresponding to O–H stretching vibration (3636 and 3549 cm^{-1}) [11], C=O stretching vibration (3473, 1766 and 1264 cm^{-1}), C–O–C stretching vibration (1140, 1096 and 1026 cm^{-1}) [12], –CH=CH₂ stretching vibration (3074 and 1650 cm^{-1}), C=C deformation vibration (964 cm^{-1}), C–H stretching vibration (2952 cm^{-1}) [13], and C–H deformation vibration (1456, 1405, 879 and 788 cm^{-1}) [14] were studied; these peaks are characteristic of the PADC film. However, the two strong absorption bands of C=O and O–C–O carbonate ester bond of PADC are saturated.

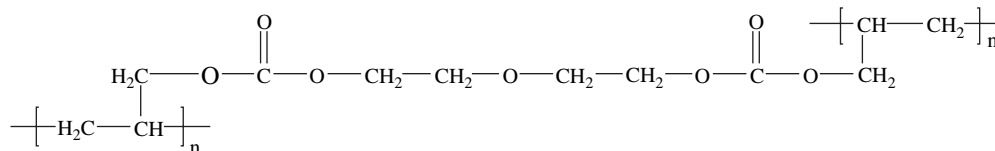


Fig. 1. The repeating unit of PADC.

Table 1
Description of the wavelengths of the three different ultraviolet sources employed for irradiation of the PADC films

	Wavelength (nm)	Wavelength with maximum intensity (nm)
UVA	340–405	377
UVA + B	300–405	374
UVC	250–263	257

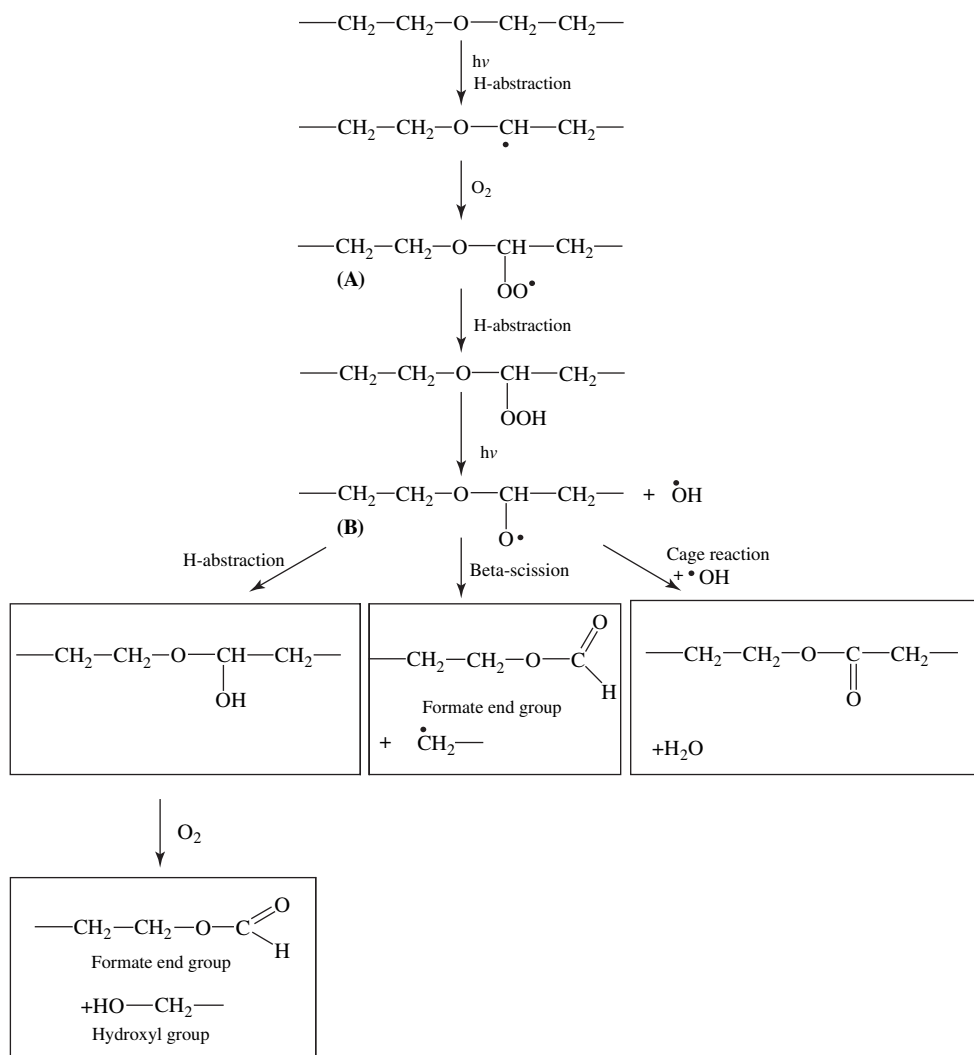
The 1650 cm^{-1} band, which signifies the $\text{C}=\text{C}$ bond, indicates the presence of the monomer left unpolymerized [15] and that the PADC does not reach full conversion of the allyl group. The degree of polymerization of PADC is relatively lower as a result of the degradative chain transfer for polymerization of the allyl group [15–17]. There is a competition between the addition of allyl radicals to the allyl group (propagation reaction) and hydrogen abstraction from the monomer (degradative chain transfer) during polymerization.

In this study, the FTIR results revealed that PADC suffered serious degradation after UVA + B or UVC irradiation.

3.2. Photochemical modifications under UV irradiation

Photo-oxidative degradation is a free radical chain mechanism (initiation, propagation, termination and chain branching) which occurs when the polymer is exposed to UV in the presence of oxygen. Chemical modifications have been attributed to scission of the polymer chains and to the formation of the cross-linkages.

The first step in the mechanisms of photo-oxidation of PADC (Scheme 1) is a hydrogen abstraction from the polymeric backbone, which causes the formation of free radicals. The formation of hydroperoxides occurs on the carbon atom in the α -position of the oxygen atom of the ether group. This mechanism involves the hydrogen abstraction from a labile hydrogen atom followed by reaction with oxygen to form peroxy radicals (A). The peroxy radical then abstracts a hydrogen atom from the macromolecular chain to form



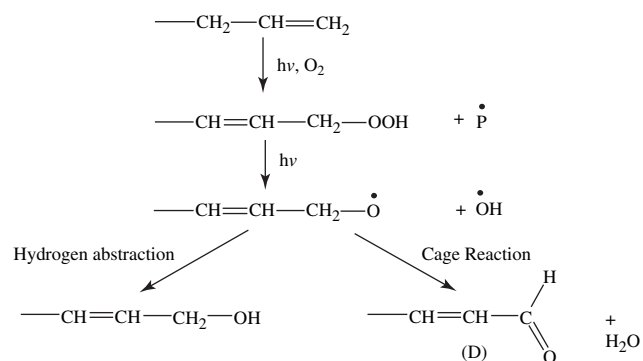
Scheme 1. Photo-oxidation at the ether group.

hydroperoxide. Hydroperoxides are unstable and rapidly decompose to form an alkoxy macroradical (B) and a hydroxyl radical after the homolysis of the hydroperoxides (O–O bond). Alkoxy radicals can undergo hydrogen atom abstraction to form hydroxyl groups, β -scission of the C–C bond to yield formate end groups and cage reaction with a hydroxyl radical to form ester groups [18].

It is suggested that the major photo-products resulting from oxidation are carbonyl and hydroxyl by-products. The formation of bonded alcohols and carboxylic acids can be observed by the increase of net absorbance around 3550 and 3473 cm^{-1} in the IR spectra, respectively. Repetition of formation of formate end groups by decomposition of hydroperoxides will cause scission of the hydrocarbon chain. During photo-oxidation in PADC, there is a reduction of the ether group which is evidenced by the decreasing net absorbance at 1140, 1096 and 1026 cm^{-1} .

The allylic group ($\text{CH}_2=\text{CH}-\text{CH}_2-$) also plays an important role in the photo-oxidative process [2]. On UV irradiation in the presence of oxygen, the formation of α,β -unsaturated hydroperoxides occurs at the α -position to the double bond of the allylic group. The formed hydroperoxides will then be converted into alcohols, ketones, carboxylic acids, etc.

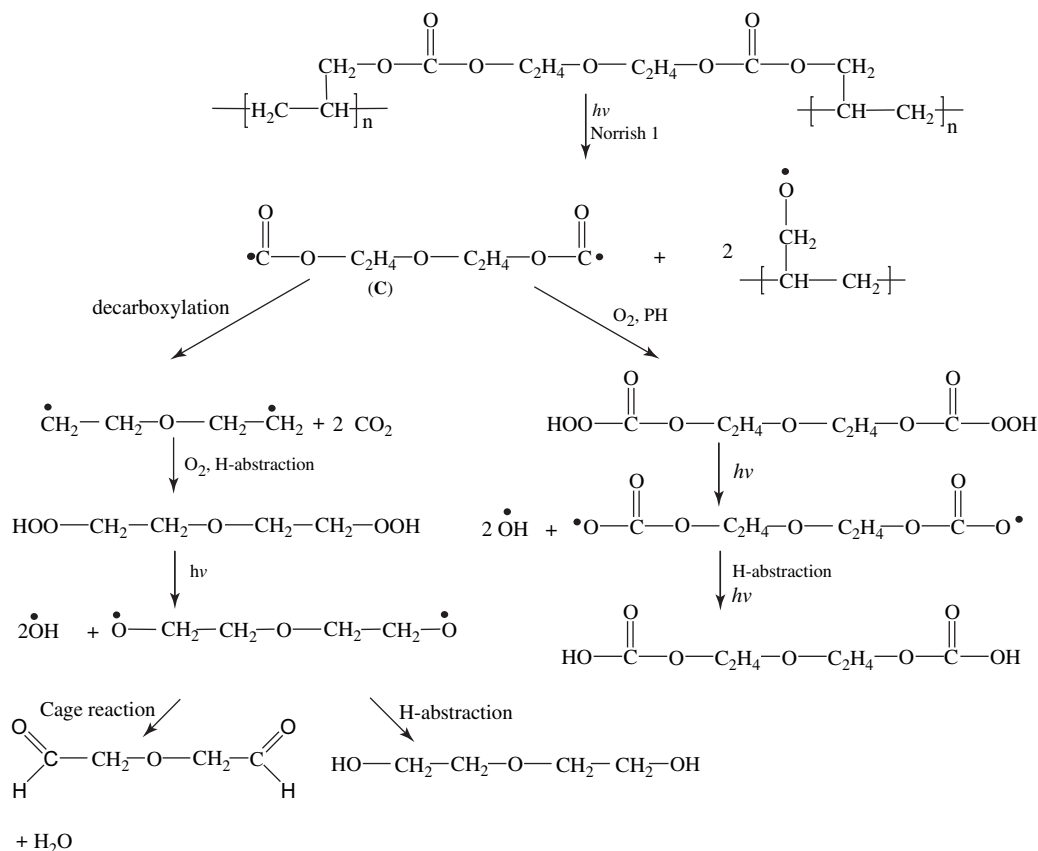
After UV irradiation, PADC can undergo the Norrish type 1 reaction [19] with the cleavage of the bond between the carbonyl group and the adjacent oxygen atom. The radicals (C)



Scheme 2. Photo-oxidation at the allylic group.

formed in CO–O scission may decarboxylate to form carbon dioxide before further radical recombination and hydrogen abstraction. As a result of the Norrish type 1 reaction, the absorption intensities at 1140, 1096 and 1026 cm^{-1} decrease.

Schemes 1–3 illustrate the possible mechanisms of photo-oxidation of PADC, which can explain the formation of the hydroxyl group and scission of the polymer chain. These can be observed in the variation of absorption in the FTIR spectra, which in turn explain the trend of V_b of PADC subjected to UV irradiation. The free radicals generated by UV radiation can combine with different radicals, resulting



Scheme 3. Photo-oxidation at the carbonyl group through the Norrish type 1 process.

in cross-linking which can be indicated by increases in the hardness and reduced modulus of the PADC films.

3.3. Photo-oxidation at UVC ($\lambda < 280$ nm)

Short-wavelength UV has sufficient energy ($111.28 \text{ kcal mol}^{-1}$) to cleave the bonds in the polymer chains with the production of free radicals [20]. The produced radicals can initiate further reactions with molecular oxygen, which result in the splitting of the macromolecular chains. Ultraviolet absorption spectra of unexposed PADC and PADC exposed for different durations from 1 to 200 h are shown in Fig. 2. It is observed that PADC has high absorptivities for short-wavelength UV irradiation. The absorption in the UV–vis region is attributed to the presence of chromophores. The strong absorption bands in the region between 200 and 240 nm are attributed to the C=C band [21]. There is an increase in the absorption at 307 nm at the beginning (3 h), which can be explained by the formation of an unsaturated group in combination with carbonyl groups [22], such as α,β -unsaturated aldehyde (D) (Scheme 2). After 3 h of UV exposure, this absorption band of double bond disappears. This can be caused by the following two types of reactions. (1) It may undergo isomerization to give β,γ -unsaturated carbonyl group, which then reacts further by the Norrish type 1 process. (2) There is a formation of cross-linking between adjacent α,β -unsaturated carbonyl groups. The destruction of the unsaturated groups leads to the continuous decrease in the intensity between 200 and 240 nm with an increase of the exposure time.

UVC in an atmosphere with oxygen causes a significant acceleration in the bulk etch rate V_b of PADC. The V_b increases with the UVC exposure time at the beginning. Fig. 3 shows V_b as a function of UVC exposure time for an etching time of 3 h. The V_b increased from 1.37 to $4.49 \mu\text{m/h}$ for UVC exposure time up to 20 h, but reached a saturation at about $4.82 \mu\text{m/h}$ for prolonged exposures to UVC.

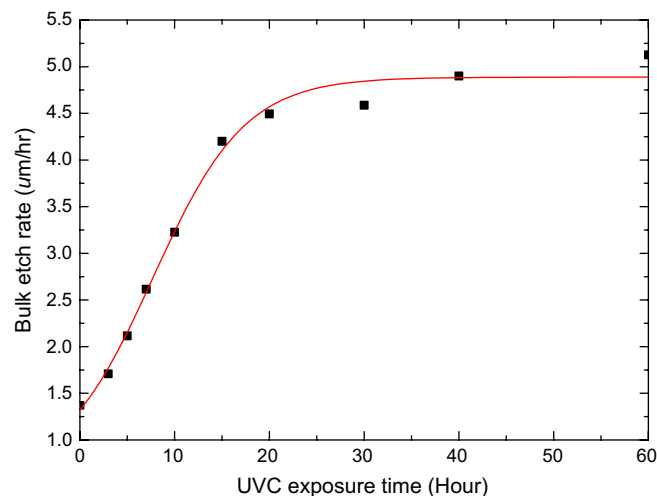


Fig. 3. The bulk etch rate of PADC for different UVC exposure durations where the etching time was 3 h.

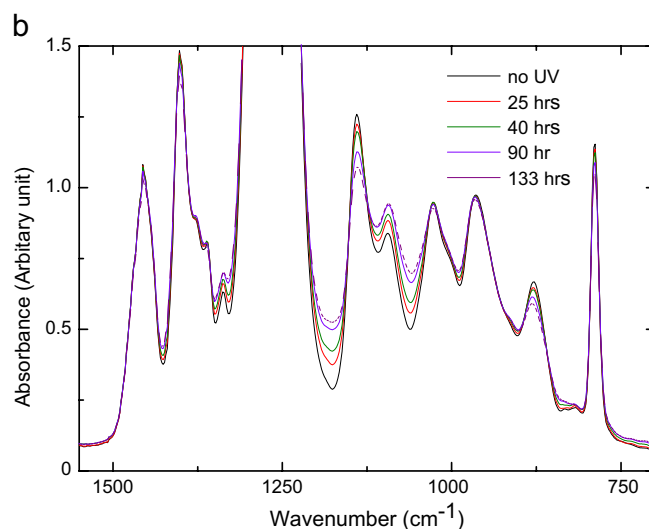
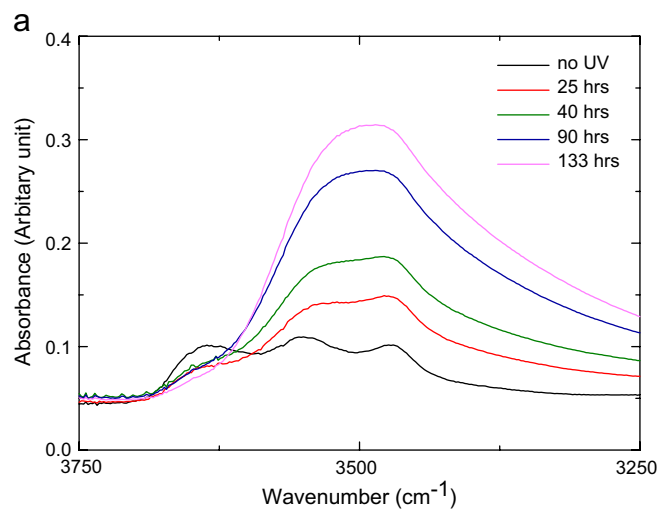


Fig. 4. FTIR spectra of $17 \mu\text{m}$ PADC before and after 25, 40, 90 and 133 h of UVC exposure in the presence of oxygen: (a) $3000\text{--}4000 \text{ cm}^{-1}$ (hydroxyl vibration region) and (b) $700\text{--}1700 \text{ cm}^{-1}$ (C–O stretching vibration region).

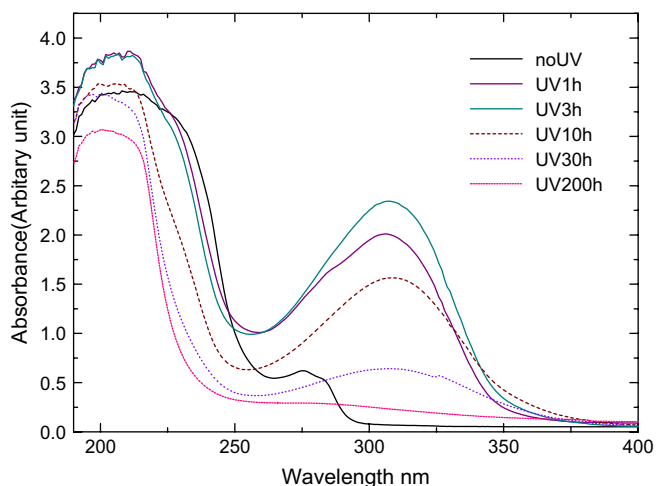


Fig. 2. UV–vis spectra of unexposed PADC samples and of PADC samples exposed to UVC for 1, 3, 10, 30 and 200 h.

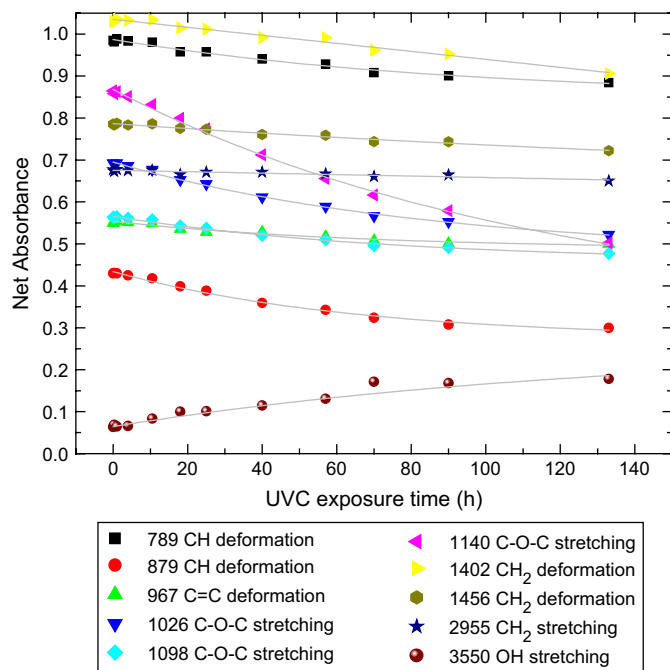


Fig. 5. The variation of net absorbance for different UVC exposure durations.

The cause of photo-degradation of PADC is primarily chain scission which can be revealed by FTIR measurements. The FTIR absorption spectra of PADC (unirradiated and irradiated with UVC) are shown in Fig. 4. Fig. 5 shows the changes in the net absorbance as a function of the UV fluence. The FTIR spectra show the main evidences of chemical degradation by UV as the intensity decrease of the infrared bands characteristic of the different chemical functional groups and the creation of hydroxyl groups.

Scission of the polymer chain reduces the average molecular weight of the detector, which increases the bulk etch rate subsequently by increasing the solubility and the diffusion rate of the etched products [16,23,24]. Formation of the hydroxyl or hydroperoxy group is also related to the bulk etch rate of PADC. Firstly, establishment of hydrogen bonds between the hydrophilic groups (OH) and the surrounding water molecules will cause the formation of a highly organized water layer around the polymer chain. Formation of saturated water contributes to the enthalpy of mixing and explains the good solubility of the polymer in sodium hydroxide solution [25]. Secondly, conversions of the hydroperoxide into alcohols and ketones cause scission of the hydrocarbon chains in PADC, which results in an increase in V_b .

However, for prolonged UVC exposures, active sites (free radicals) created by scission may lead to intermolecular cross-linkings. The fragments may link to the main chain of a neighboring molecule to give a branched molecule of a higher molecular weight. Therefore, on prolonging the UVC exposure, a cross-linked protective layer can be formed, which increased the hardness and reduced the modulus of the polymer [26,27]. In the first 60 h of UVC exposure, the measured values of the hardness and reduced elastic modulus are increased from 0.197 to 0.248 GPa and from 3.00 to

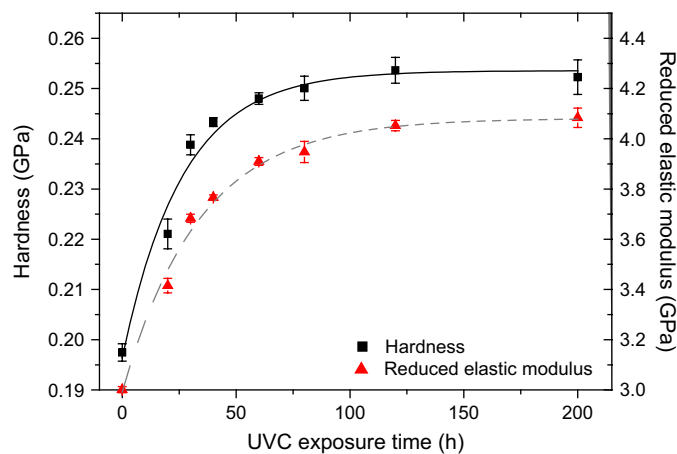


Fig. 6. The variation of the hardness and reduced modulus as a function of UVC exposure duration.

3.91 Gpa, respectively, as shown in Fig. 6. Our chemical analysis indicates that both scission and cross-linking occur simultaneously. However, the increase in the bulk etch rate is correlated to the process of scission. This result suggests that the chain scission is a dominant process at the beginning.

However, both the hardness and the reduced modulus have reached saturation after 60 h of UVC exposure. The rates of scission of different functional groups also saturate after about 60 h of UVC exposure as shown in Fig. 7. For the sake of clarity in showing the non-linear scission rates of the chemical bonds, only the most significant absorption bands, viz., 879 cm^{-1} (deformation of C–H), 1140 cm^{-1} (stretching of C–O–C), 2955 cm^{-1} (stretching of C–H) and 3550 cm^{-1} (stretching of O–H), are shown in Fig. 7. The saturation of V_b for increased exposure time can also be explained by the formation of a superficial cross-linked layer. It is believed that the cross-linked layer of PADC will hinder the penetration

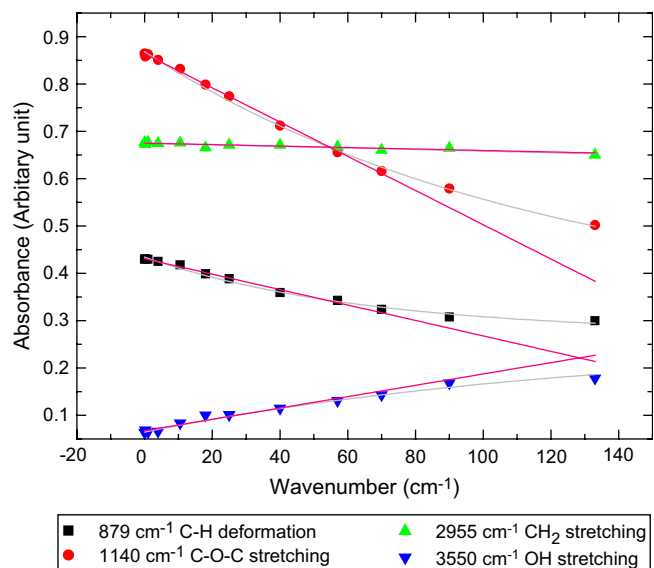


Fig. 7. The variation of net absorbance for different UVC exposure durations.

of oxygen [28] and will also retard the scission rate so that V_b no longer increases at higher UVC exposures.

In the presence of oxygen, irradiation of PADC by UV at shorter wavelengths leads to prominent changes in the FTIR spectra and nano-hardness measurement results. The FTIR studies confirm the scission of the functional groups such as C–C, C–H and C–O, as well as the formation of OH and OOH groups after UV exposure, which enhances the V_b of PADC. The nano-mechanical studies suggest that cross-linking is a reaction leading to increases in the hardness and reduced elastic modulus, and thus to retarded degradation rates.

3.4. Photo-oxidation at UVA + B ($\lambda > 300$ nm)

The absorption of long-wavelength UV ($\lambda > 300$ nm) by PADC is relatively low. This suggests that direct photochemical processes are not prevalent at wavelengths longer than 300 nm. The initiation of photo-oxidation of PADC is due to hydroperoxide photolysis. The long-wavelength photo-oxidation of polymers is initiated by the chromophoric groups which are attributed to the conjugated system of bonds, such as C=C and C=O bonds. The active radicals will then initiate photo-degradation by abstraction of hydrogen from the polymer backbone. This photo-induced oxidation leads to the formation of macroradicals which are further oxidized into the hydroperoxides. The hydroperoxide group may undergo homolysis to form both alkoxy and hydroxyl radicals which can undergo hydrogen abstraction, β -scission and cage reaction.

Fig. 8 shows that the net absorbances at 789, 879, 967, 1026, 1098, 1140, 1402, 1456 and 2955 cm^{-1} decrease with the UVA + B exposure time, which implies the occurrence

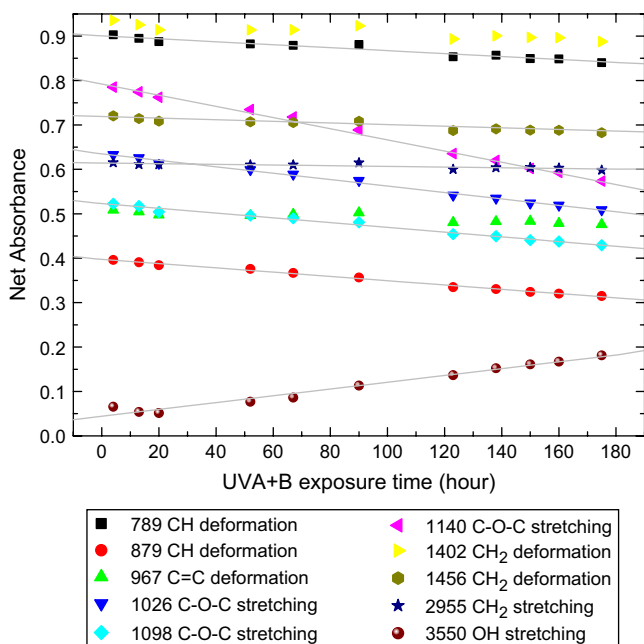


Fig. 8. The variation of net absorbance for different UVA + B exposure durations.

of scission of the polymer chain. An increase in the net absorbance is also observed in the range from 3100 to 3700 cm^{-1} , which implies the formation of hydroxyl (OH) and hydroperoxy (OOH) groups during photo-degradation. The FTIR results hint that V_b should become larger as the UV exposure time prolongs. In fact, the V_b shown in Fig. 9 increases to 5.73 $\mu\text{m}/\text{h}$ for 40 h of UV exposure when the etching time is 3 h.

3.5. Photo-oxidation at UVA ($\lambda > 340$ nm)

There are no changes in the net absorbances, which imply that UVA causes no effects on scission and cross-linking. There is no chemical modification of the polymer, which implies that there is no increase in the bulk etch rate with the UV exposure time. In fact, no observable variations in V_b can be found with the increasing UV exposure time. The V_b remains constant at about 1.39 $\mu\text{m}/\text{h}$ with UVA exposures up to 30 h when the etching time is 3 h.

3.6. Photo-oxidative degradation with UVC

As described above, oxygen plays an important role in photo-degradation. The PADC films subjected to different UVC exposures have been etched in 6.25 N NaOH/H₂O. The V_b values of PADC for etching time 0.5, 1 and 3 h are shown in Fig. 10. From Fig. 10, we see that the saturated V_b values are 20.90, 11.25 and 4.82 $\mu\text{m}/\text{h}$ for etching time of 0.5, 1 and 3 h, respectively. The decreasing saturated V_b values with increasing etching time imply that V_b is decreasing with the depth. The V_b values shown in Fig. 10 are calculated from the actual removed layer per unit etching time, which are the average values of the depth dependent V_b values. The V_b values of PADC under UVC exposures have been found to accelerate significantly towards the exposed surface. The

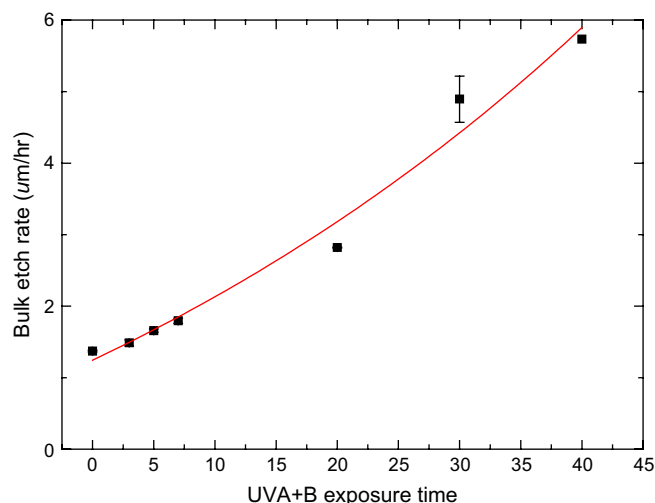


Fig. 9. The bulk etch rate of PADC for different UVA + B exposure durations where the etching time was 3 h.

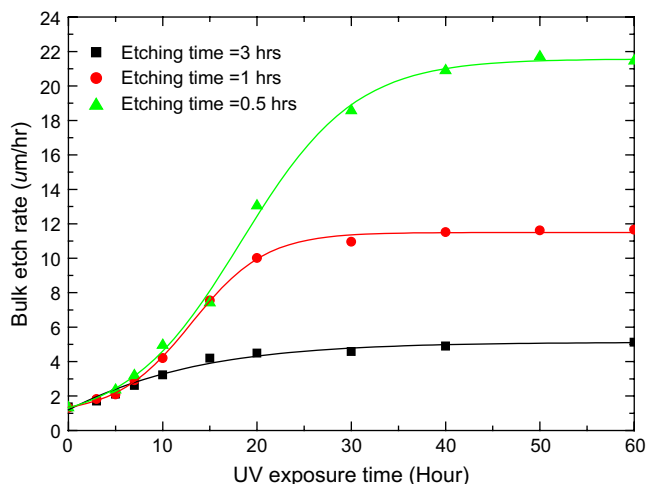


Fig. 10. The variation of the bulk etch rate V_b as a function of UVC exposure duration with three different etching times of 0.5, 1 and 3 h.

variation of V_b with the depth is due to the limited penetration of oxygen into deeper regions [2].

The PADC films were exposed to UVC for 30 h and they were then etched for different periods. Figs. 11 and 12 show the variation of the removed layer and the variation of V_b as a function of etching time, respectively. Under the same UVC exposure, V_b was found to decrease dramatically from 12 to 1.5 $\mu\text{m}/\text{h}$. The results indicate that the penetration depth of UVC-radiation in PADC is about 10.5 μm . In air, extensive photo-oxidation occurs resulting in the extremely large V_b for the surface of the PADC film, but the remaining bulk material is left largely unmodified.

4. Conclusions

The photochemical changes of PADC under UV irradiation with different wavelengths have been investigated in this study.

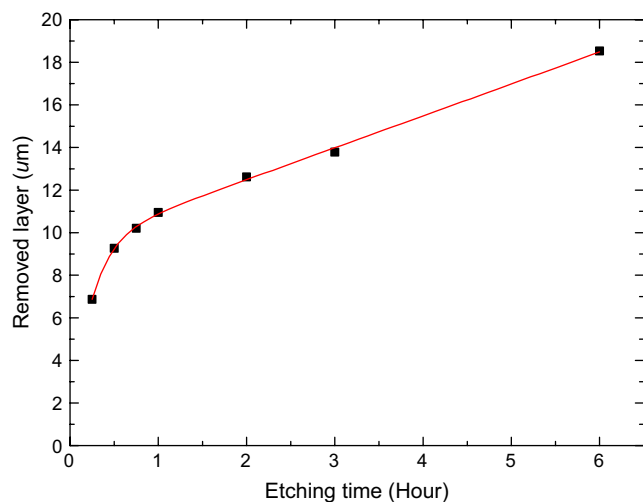


Fig. 11. The changes of the removed layer of PADC films exposed to UVC for 30 h as a function of etching time.

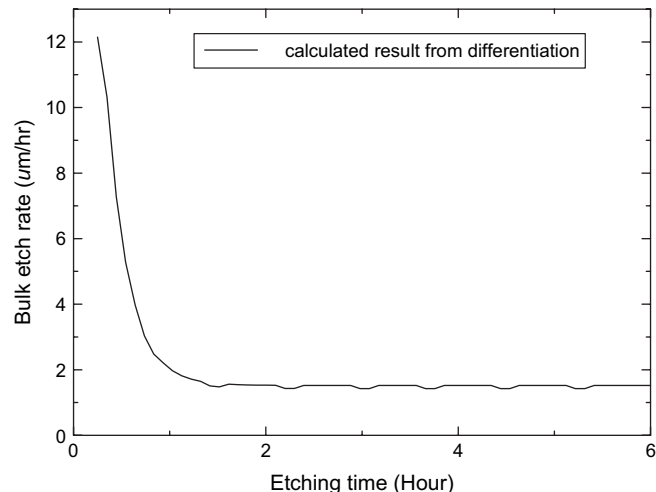


Fig. 12. The calculated results from differentiation of changes of the removed layer of PADC films which have been exposed to UVC for 30 h as a function of etching time.

It has been found that UVA causes no changes in both the net absorbance in IR spectra and the V_b values. The IR spectra indicated that there was scission of bonds and formation of hydroxyl group under both UVA + B and UVC exposures. UV irradiation will promote chemical modifications in PADC. The V_b increases with UVA + B and UVC exposures. However, for prolonged UVC exposures, V_b will no longer increase because of the formation of a cross-linked layer on the surface of the PADC film. Scission of polymer chains and the formation of hydroperoxide can enhance V_b . However, cross-linking will hinder the degradation rate. The V_b has also been found to vary with depth of the PADC film because of the different amounts of oxygen diffused into the PADC film.

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