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Poly(ethylene 2,6-naphthalate) (PEN) was treated with ozone in the absence of radiation and the results were compared with ultraviolet (UV) photooxidation using 253·7 and 184·9 nm radiations. The surface modification of the top 2–5 nm was analyzed by X-ray photoelectron spectroscopy (XPS) for chemical changes. Higher saturation levels of oxidation were achieved using UV photooxidation than ozonation. Both treatment methods increased the amounts of C–O–C, C=O and O–C=O bondings while UV photooxidation also increased the concentration of the anhydride/carbonate moieties on the surface. Atomic force microscopy detected smoother surfaces with increasing treatment time for both the treatments. The changes in functional groups and surface roughness with both treatments contributed to an increase in hydrophilicity as determined by advancing water contact angle measurements. A greater increase in hydrophilicity was observed for the UV photooxidized PEN samples. Initial results showed a slight increase in hydrophilicity when acrylic acid was grafted onto ozone-treated PEN surfaces, although, the ester group in the PEN structure made it difficult to detect poly(acrylic acid) by XPS.

1.   Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a transparent polymer defined by a large aromatic polyester chain as shown in Figure 1.

The naphthalate ring on the main chain contributes to the high degree of stability due to the delocalization effects associated with its aromaticity. The chemical structure of PEN causes the polymer to absorb radiation well in the near-ultraviolet (UV) region, exhibit a high gas barrier, make it resistant to many dilute acids and solvents and possess very good thermal and mechanical properties. These physical properties make PEN a suitable material for flexible electronic applications, solar cells, food packaging, quality fibers, magnetic recording tape, printed circuit boards, liquid crystal displays, organic light-emitting diode devices, bottle fabrication material and a stable blending material with other polymers.[1–9]

Similar to polystyrene, discarded PEN in landfill sites has limited capacity for water absorption and its physical and chemical properties make it relatively inert and virtually unaffected by naturally occurring degrading agents and sources.[10] In order to achieve good adhesion in certain applications, UV photooxidation has been used to modify the PEN surface and increase wettability.[2,11–13] The surface modification during UV photooxidation may be initiated by UV radiation, O atoms and/or ozone. In this study, PEN was surface modified with ozone in the absence of radiation and the results are compared to treatment with UV photooxidation. Attempts were made to polymerize acrylic acid and CH_2=CH–COOH to form the grafted hydrophilic poly(acrylic acid) (PAA)[14] on the treated samples and improve the surface hydrophilicity.

X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and advancing water contact angle were used to analyze the changes in surface composition, surface roughness and hydrophilicity, respectively.

2.   Experimental

2.1   Materials

A coil of poly(ethylene 2, 6-naphthalate), which was previously used as a footage marker of an inkjet printer, was cleaned using

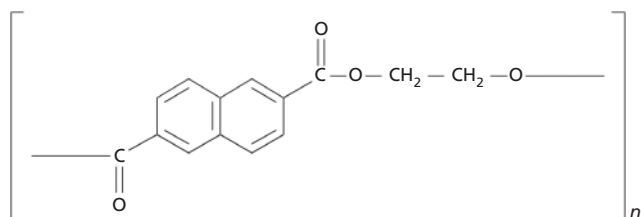*Corresponding author e-mail address: gatsch@rit.edu

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Figure 1. Molecular structure of poly(ethylene 2,6-naphthalate)

carbon dioxide snow cleaning along with acetone and isopropanol sonication. Each specimen of PEN was cut to a rectangular size of 1.5×2 cm and a small mark was made in the upper right corner to point out the surface-modified side of PEN. Before treatment, the samples were washed and degreased in an ethanol bath at room temperature for 10 min. The specimens were then dried in a vacuum hood.

2.2 Ozone generator

The PEN sample was placed in a pyrex cell located downstream from the ozonizer which consisted of a Rayonet photochemical chamber (manufactured by Southern New England Ultraviolet Co., Inc., Branford, CT) having 16 low-pressure mercury lamps which emit both 184.9 and 253.7 nm photons with an intensity ratio of about 1:6.[10] A cylindrical photochemical cell (2.54-cm dia., 17.8-cm long) was constructed of Suprasil (Heraeus Quartz America LLC, Buford, GA) quartz, fitted with a Cajon removable high-vacuum stainless steel fitting, and placed inside the chamber.[10] High-purity nitrogen and oxygen (99·99%) were flowed through the chamber and photochemical cell for at least 10 min at flow rates of c. 5×10^3 and 43 sccm, respectively, to displace air prior to the ignition of the radiation source.

Molecular nitrogen is transparent to the UV radiation while ground-state oxygen molecules absorb 184.9 nm photons which have sufficient energy to dissociate the oxygen molecules into O atoms.[15] Ozone is formed in the photochemical cell at atmospheric pressure by the reaction of O atoms with molecular oxygen and a stabilizing molecule, and then transported c. 40 cm downstream to react with the PEN sample in the absence of the radiation. For the UV photooxidation studies, the PEN sample was placed in the photochemical cell located in the chamber. Since ozone is linked to a broad array of health threats,[16] the exiting gas was passed through a solution of saturated potassium iodide to remove ozone prior to emission into the vacuum hood.

2.3 Graft polymerization

Following ozonation and UV photooxidation, the surfaces were graft polymerized with an aqueous solution of acrylic acid (6.8 M) in a round-bottom flask. Beforehand, acrylic acid stabilized with 0.02% hydroquinone monomethyl ether, purchased from Fluka, was distilled out under reduced pressure. The acrylic acid water solution

PEN sample, treatment time: min	Atomic % of C	Atomic % of N	Atomic % of O	O/C ratio
Not cleaned, 0	78	0·2	21·8	0·28
*Cleaned untreated, 0	77	0·2	22·8	0·30
*Cleaned untreated, 0	77·3	0	22·7	0·29
15	75·1	0·5	24·4	0·32
30	73·4	0·5	26·1	0·36
90	71·6	0·7	27·7	0·39
120	71·1	0·8	28·1	0·40
180	69	1·1	29·9	0·43
240	70·7	0·7	28·6	0·40
300	70·1	0·8	29·1	0·42

*Replicate samples

Table 1. Quantitative XPS results for PEN treated with ozone

in a round-bottom flask was purged with dry argon for 15 min, then iron sulfate heptahydrate and l-ascorbic acid were added so that the concentrations of Fe^{2+} ions and ascorbic acid were 0.010 and 0.014 M, respectively, in the reaction system. The ferrous ions act as a reducing agent for decomposition of oxygen-containing functional groups, such as peroxides and hydroperoxides, fixed on the surface to produce grafted radicals and, as a result, minimize the formation of free radicals in the surface area. Ascorbic acid is used as a co-reducing agent in the reduction of ferric ions back to ferrous ions.[17] Grafting was conducted at 65°C while purging with argon for 1.5 h. After the reaction was complete, the PEN samples were collected, washed with hot deionized water, heated in deionized water at 65°C for 2 h to remove non-grafted monomer and polymer and then dried in a desiccator to constant mass.[10,18] The reaction conditions such as the monomer concentration, temperature and duration have been previously described in detail.[19]

2.4 X-ray photoelectron spectroscopy

The PEN sample was mounted on a microscope coverslip and placed directly in the XPS sample holder beneath a molybdenum mask. A region of about 800 μm in diameter was analyzed with a Physical Electronics Model 5800 XPS that examined the top 2–5 nm of a sample's surface using a take-off angle of 45° between the sample and analyzer. The monochromatic Al Kα (1486 eV) X-ray beam irradiated the sample and the electron optics of the analyzer was focused to accept only photoelectrons emitted from PEN. The quantitative analyses are precise to within 5% for major constituents and 10% for minor constituents. The samples were

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Treatment time: min	Atomic % of C	Atomic % of N	Atomic % of O	O/C ratio
Cleaned, 0	75·7	0·3	24	0·32
5	71·2	0·4	28·4	0·4
15	69·5	0·5	30	0·43
30	68·5	0·6	30·9	0·45
60	65·9	0·7	33·4	0·51
90	65·2	0·8	34	0·52
120	66·9	0·8	32·3	0·48

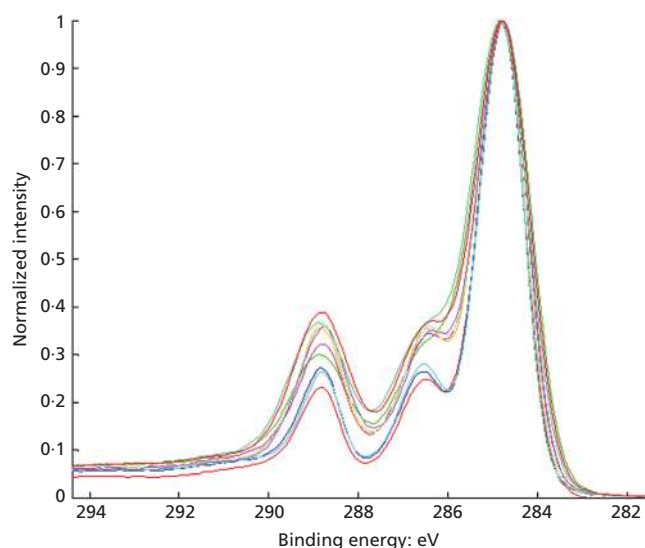**Table 2.** Quantitative XPS results for PEN treated with UV photooxidation

Figure 2. C 1s spectra for ozone-treated PEN as a function of treatment time. The arrow shows increasing treatment time from 0 to 300 min

Figure 3. Overlapped C 1s spectra for untreated and UV photooxidized PEN as a function of treatment time. The arrow shows increasing treatment time from 0 to 120 min

A material's balance was calculated to test if the results of the curve fitting agreed with the concentrations as determined from the quantitative analyses.

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2.5   Atomic force microscopy

Surface roughness was determined using a Bruker DI3000 Atomic Force Microscope (AFM) in the tapping mode. For each specimen, a 5 × 5μm image was obtained using the same Olympus OTESPA tip.

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2.6   Contact angle goniometry

The water contact angles on the PEN films were measured using a Rame-Hart model 200 standard goniometer. The samples were placed on a clean and pre-balanced stage. A 10-μl syringe was used to deposit deionized water droplet on the surface. An advancing contact angle mode was utilized by recording the contact angle as 10 μl of water was gradually added. The angle was measured using a high-resolution camera with the Drop Image Advanced Software.[20]

3.   Results

3.1   XPS results for ozonation and UV photooxidation of PEN

The elemental survey scans from 0 to 1200 eV binding energy detected mainly carbon and oxygen, with trace amounts of nitrogen (Tables 1 and 2). The atomic percentages (at.%) for cleaned and untreated samples were within experimental error of the stoichiometric composition for PEN (77·8 and 22·2 at.% of C and O, respectively).

charge neutralized with a flood of low-energy electrons from a BaO field emission charge neutralizer. This method of analysis minimized radiation damage to the samples. The samples were analyzed both before and after each treatment.

Curve fitting of the C 1s spectra was performed using the C 1s spectrum for a cleaned and untreated PEN sample as the initial model. The process was to subtract the control spectrum from that of the treated sample. The remainder spectrum was curve fitted to determine the number of peaks, their binding energies and peak widths resulting from treatment. The peaks obtained from curve fitting the remainder spectrum were used to curve fit the total treated spectrum. Any missing peaks, such as weak energy loss peaks, are then added to the curve fitting of the treated sample to achieve a good chi-square fit.
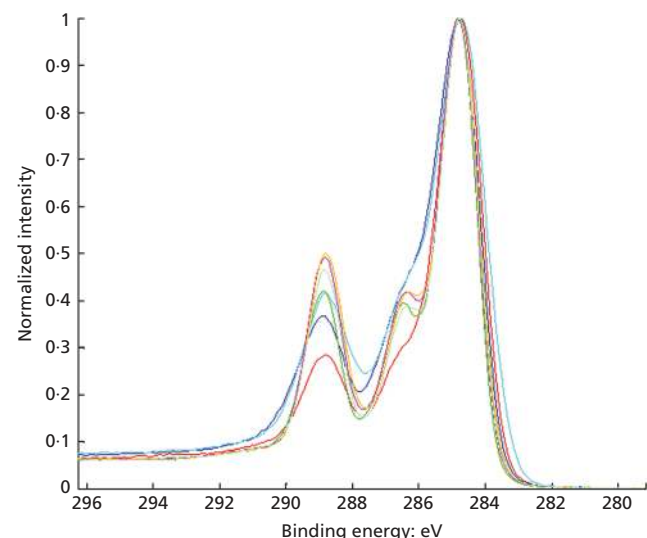
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Binding energy: eV	Assignment
284·7	C–C sp^2
285·1	C–C sp^3
286	C-O-C, C━C (epoxide)
287	C=O
288·6	O–C=O
289·8	O=C–O–C=O, O–(C=O)–O
292	Energy loss

Table 3. XPS C 1s binding energies and their assignments[21]

For each treatment method, at least two sets of experiments were done with increasing treatment time. As shown in Tables 1 and 2, the oxygen concentration increases to saturation levels of c. 30 and 34 at.%, for ozonation and UV photooxidation, respectively. Shorter treatment time was required to reach saturation using UV photooxidation than ozonation.

The overlapped C 1s spectra for the untreated and treated samples are illustrated in Figures 2 and 3. The peaks in the C 1s spectra are due to carbon–carbon and carbon–oxygen bonding environments. Peak assignment for the untreated and treated samples was accomplished by curve fitting the spectra using the binding energies of the individual components of the spectra which are summarized in Table 3.[21] With increasing treatment time, the curve fitting results (Tables 4 and 5) show a decrease in sp^2 and sp^3 C–C bondings and

Treatment time: min	Not cleaned, 0	*Cleaned, 0	*Cleaned, 0	15	30	90	120	180	240	300
C–C sp^2	48·2	44·5	46	44·6	45·2	40·2	40·5	41·3	39	42·7
C–C sp^3	20·5	21·2	19·2	17·2	11·1	15·6	14	10·8	10·8	8·4
C-O-C, C━C (epoxide)	1·3	1·1	2·7	5·1	8·4	6	7·1	8·5	9·1	8·3
C=O	15·6	16·3	16·3	15	15·9	17·4	16·9	16·6	19·6	18
O–C=O	8·6	10·1	9·9	12	12·8	15·2	16	18·7	15·7	18·2
O=C–O–C=O, O–(C=O)–O	5·4	5·9	5	5·2	5·5	4·9	4·5	3	5·1	3·7
Energy loss	0·5	0·9	0·9	1	1·1	0·8	1	1	0·8	0·9

*Replicate samples

**Table 4.** C 1s curve fitting areas in percentage as a function of treatment time with ozone

Treatment time: min	Cleaned, 0	5	15	30	60	90	120
C–C sp^2	47·9	40·3	39·4	33	35·4	32·2	40·5
C–C sp^3	16·3	11·4	12·7	14·7	13·6	13	9·2
C-O-C, C━C (epoxide)	3·3	6·3	5·7	6·9	6·7	8·8	6·5
C=O	13·9	18·9	18·2	21·5	19	19·3	18·2
O–C=O	11	12·3	14·2	14·9	15·9	17·7	15·2
O=C–O–C=O, O–(C=O)–O	5·5	8	7·4	6·8	7·8	7·1	8·8
Energy loss	2·2	2·8	2·5	2·2	1·6	1·9	1·7

Table 5. C 1s curve fitting areas in percentage for PEN as a function of treatment time with UV photooxidation

PEN sample, treatment time: min	Atomic % of C	Atomic % of N	Atomic % of O	O/C ratio
PAA grafted, 0-min treatment	74·4	0·2	25·4	0·34
PAA grafted, 30-min O_3 treatment	75	0	25	0·33
PAA grafted, 90-min O_3 treatment	73·1	0·5	26·4	0·36
PAA grafted, 150-min O_3 treatment	73·4	0·4	26·2	0·36

Table 6. Quantitative XPS results of PAA grafted ozonized PEN

PEN sample, treatment time: min	Atomic % of C	Atomic % of N	Atomic % of O	O/C ratio
PAA grafted, 0-min UV treatment	74·3	0·5	25·2	0·34
PAA grafted, 15-min UV treatment	72·5	0·2	27·4	0·38
PAA grafted, 30-min UV treatment	72·4	0·1	27·5	0·38
PAA grafted, 90-min UV treatment	72·1	0·4	27·5	0·38

Table 7. Quantitative XPS results for PAA grafted UV photooxidized PEN

an increase in the amounts of C–O–C, C=O and O–C=O moieties. UV photooxidation (Figure 3 and Table 5) also displays an increase in the concentration of the anhydride/carbonate moieties at a binding energy of 289·8 eV.

The O 1s spectra (not shown here) were broad Gaussian peaks that made it difficult to extract information concerning the carbon–oxygen bonding. Due to the lack of energy resolution of the peaks, the O 1s spectra did not provide much additional information already obtained from the C 1s spectra.

3.2 Grafting acrylic acid onto the surface-ozonized PEN

The XPS quantitative analysis results for grafting PAA to the surface modified PEN are shown in Tables 6 and 7.

The at.% of O and O/C ratios after grafting (Tables 6 and 7) show lower values at the same treatment times than observed in Tables 1 and 2, respectively.
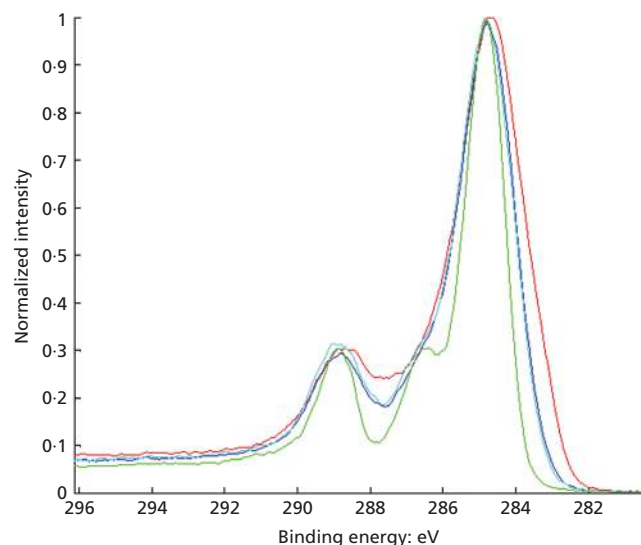

Figure 4. Overlapped C 1s spectra for untreated- and ozone-treated PEN after grafting with PAA as a function of treatment time. The arrow shows increasing treatment time from 0 to 150 min
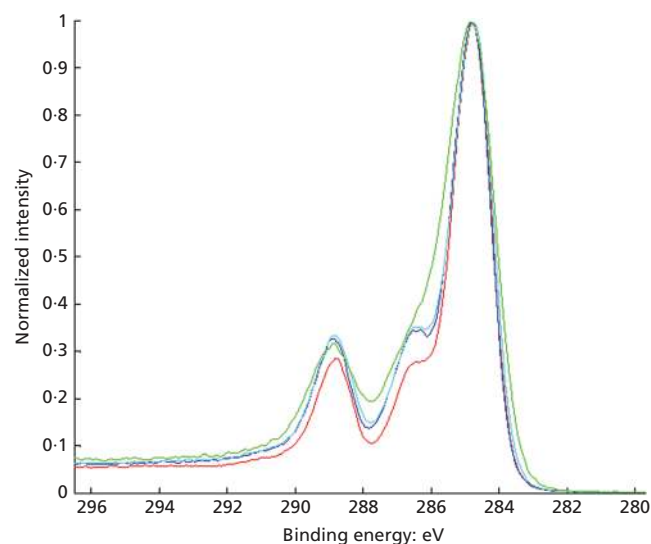

Figure 5. Overlapped C 1s spectra for untreated and UV photooxidized PEN after grafting with PAA as a function of treatment time. The arrow shows increasing treatment time from 0 to 90 min

Figures 4 and 5 illustrate the C 1s spectra of PAA grafted to untreated and treated PEN with ozone and UV photooxidation, respectively. Because of the ester group in the PEN structure (Figure 1), it is more difficult to detect PAA by XPS on the treated PEN sample compared to oxidized polysulfonic acid membrane (Nafion-117)[17] and polystyrene.[18] The curve fitting results for Figures 4 and 5 are presented in Tables 8 and 9, respectively.

Treatment time: min	Cleaned, 0	30	90	150
C–C sp^2	56·1	42·7	40·1	40·7
C–C sp^3	8·4	19	23·5	22
C-O-C, C—C (epoxide)	9·3	12·9	9	9·4
C=O	8·4	5·8	7·1	7·2
O–C=O	13·9	14·4	15·5	14·1
O=C–O–C=O, O–(C=O)–O	3·5	4·2	4·3	5
Energy loss	0·5	1	0·6	0·6

Table 8. C 1s curve fitting areas in percentage for untreated and ozone treated PEN after grafting with PAA as a function of treatment time

Treatment time: min	Cleaned, 0	15	30	90
C–C sp2	52·7	44·7	45·3	44·9
C–C sp3	16·2	15·9	12	13
C-O-C, C—C (epoxide)	7·6	8	9·5	8·6
C=O	6	11·6	13·3	13·4
O–C=O	13·7	15·1	15·3	15·5
O=C–O–C=O, O–(C=O)–O	3·6	4·6	4·3	4·5
Energy loss	0·1	0·1	0·3	0·1

Table 9. C 1s curve fitting areas in percentage for untreated and UV photooxidized PEN after grafting with PAA as a function of treatment time

The overlapped O 1s spectra were again broad Gaussian peaks making it difficult to extract information concerning the carbon–oxygen bonding.

So far, only two measurements were made of the water contact angles for PAA-ozonized samples after 30- and 90-min treatment times (56° and 50°, respectively) which showed an increase in hydrophilicity compared to the ozonated samples at these treatment times (63° and 57°, respectively).

3.3 Surface topography for ozonation and UV photooxidation of PEN

Figure 6 shows the surface topography after treatment with ozone for 0, 15, and 180 min. The root mean-squared roughness parameter (R_q) values are 3·27, 1·60 and 1·66 nm, respectively, with increasing treatment time. Thus, ozonation reduces R_q making the surfaces smoother.

Figure 7 shows the surface topography after UV photooxidation treatment for 0, 15 and 180 min. The root mean-squared roughness parameter (R_q) values are 2·03, 1·31 and 1·28 nm, respectively, with increasing treatment time. Thus, UV photooxidation also reduces R_q making the surfaces smoother.

3.4 Contact angle results for ozonation and UV photooxidation of PEN

The average advancing water contact angle for the PEN samples before treatment was c. 75°. As displayed in Figures 8 and 9, UV photooxidation resulted in about twice the percentage decrease in water contact angle, that is, increase in hydrophilicity as compared to ozonation.

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4. Discussion

Gas-phase ozonation of PEN results in an increase in oxidation with treatment time of the top 2–5 nm of the surface to achieve

10·0 nm
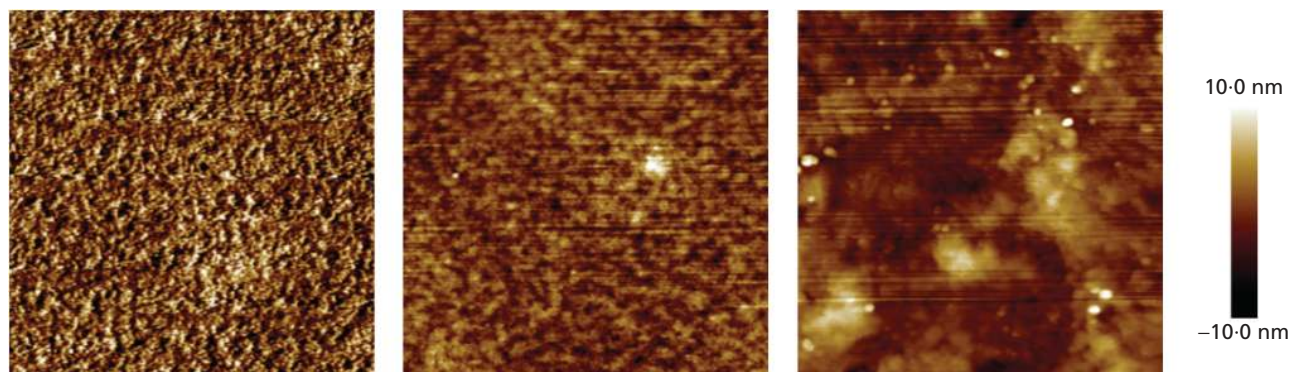
−10·0 nm

Figure 6. Surface topography after ozonation treatment (a) 0 min, R_q = 3·27 nm; (b) 15 min, R_q = 1·60 nm; (c) 180 min, R_q = 1·66 nm
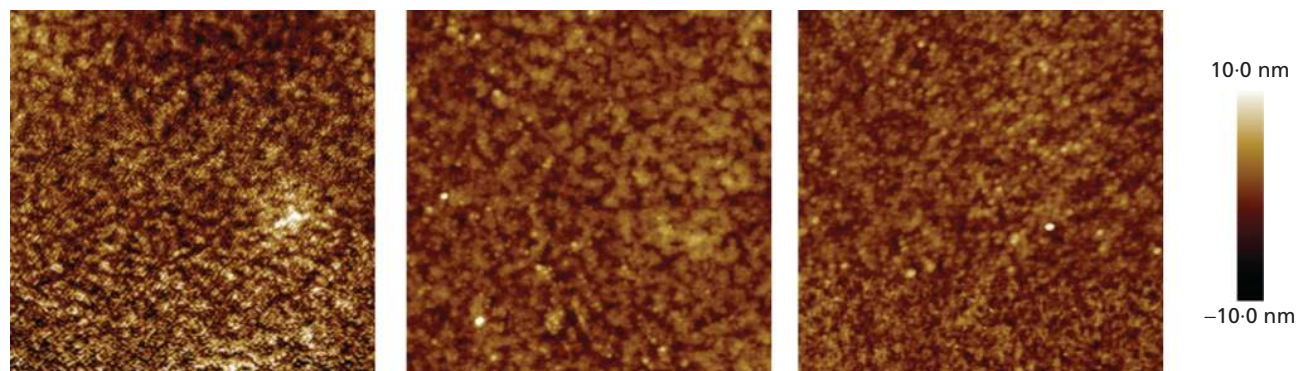
Figure 7. Surface topography after UV photooxidation treatment
(a) 0 min, R_q = 2·03 nm; (b) 15 min, R_q = 1·31 nm; (c) 180 min,
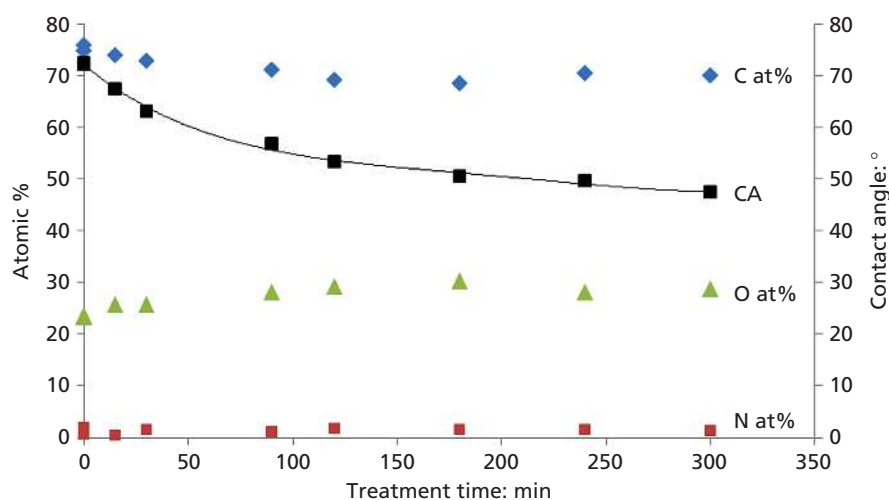R_q = 1·28 nm

Figure 8. Quantitative XPS analysis results (at.%) and contact angle
(CA) measurements for PEN treated with ozone as a function of
treatment time

a saturation level of c. 30 at.% of O. Curve fittings of the C 1s XPS spectra (Table 4) show an increase in the formation of C–O–C as ether and/or epoxy groups, C=O and O–C=O, and a decrease in C–C sp^2- and sp^3 bondings with exposure time. Ozone is well known to oxidize across unsaturated sp^2 bonds to form epoxy groups[22] as has been observed in the oxidation of benzene,[23] polystyrene,[10] and graphite.[24,25] Initially, the addition of ozone reduces sp^2 hybridization by producing a primary ozonide that undergoes sp^3-hybridized bond cleavage to form a carbonyl-containing compound and a Criegee intermediate.[22,26,27] One of the mechanisms for decomposition of the Criegee intermediate results in the formation of ester groups (O–C=O) and the release of gaseous carbon dioxide.[22]

A higher saturation level of oxidation (c. 34 at.% of O) is achieved with UV photooxidation of PEN probably because of the interaction of UV radiation and O atoms with the surface. UV radiation is well absorbed by PEN[28,29] resulting in primarily a surface effect using UV eximer lasers.[2] UV photooxidation also results in surface modification, as observed by ultraviolet–visible and Fourier transform infrared spectroscopy, showing the formation of carbonyl and anhydride groups[2,11] in agreement with the XPS analysis in this study. Decomposition of the highly oxidized moieties, anhydrides and carbonates results in both carbon dioxide evolution and formation of non-volatile carbonyl products.[2] XPS analysis of UV–ozone-treated PEN shows a decrease in aromatic C–C bonds due to the formation

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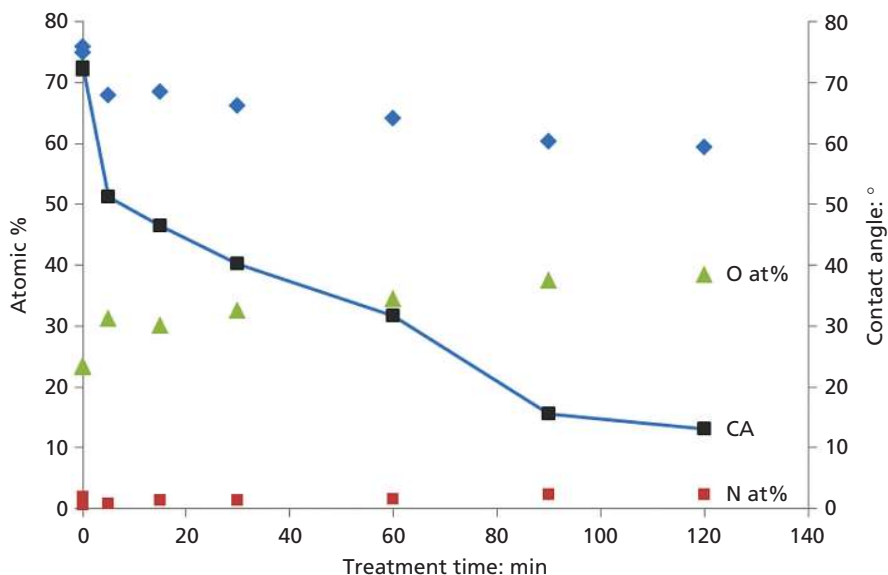Abdulal, Bailey, Mehan *et al*.

Figure 9. Quantitative XPS analysis results (at.%) and contact angle
(CA) measurements for PEN treated with UV photooxidation as a
function of treatment time

of the oxygen-containing groups, C–O–C, C=O and O–C=O,[12] as observed in this study, which enhances the wettability for successful adhesion of rare-earth ion-doped nanoparticle films.[13]

The decrease in the aromatic structure, C–C sp^2, and increase in the concentrations of the carbonyl and ester moieties during UV photooxidation of PEN may also arise from the addition of O atoms to aromatic C bonds to form triplet biradicals which may then follow one of the three pathways: (*a*) rearrangement to produce a carbonyl compound, (*b*) ring closure to form an epoxide, or (*c*) decomposition into free radicals.[30,31] The O-containing triplet biradical may react with O_2 to form a Criegee-like intermediate which rearranges to give the carbonyl and ester moieties.[32]

Oxidation of PEN and formation of oxygen-containing functional groups as well as the smoother surface contribute to the enhanced wettability of the treated PEN surface.

Probably, the low-molecular weight materials, which were formed by oxidation with the elimination of carbon dioxide, were washed away during the grafting accounting for the decrease in at.% of O and O/C ratio after grafting. A thick PAA layer would have an O/C ratio of 0·67. Curve fitting of the C 1s spectra for the samples grafted with PAA, as expected, shows a slightly larger increase in the ester group using the UV photooxidation treatment method than ozonation, although, the detection of grafting on the surface by XPS is difficult because of the ester groups in the bulk PEN.

5. Conclusion

XPS surface analysis of the treatment of PEN with an ozone and molecular oxygen mixture in the absence of radiation shows an increase in oxidation and the formation of C–O–C, C=O and O–C=O bondings. In contrast, UV photooxidation, which also may expose PEN to UV radiation and O atoms, achieved a higher oxidation saturation level and the additional formation of anhydride/carbonate moieties. Advancing water contact angle measurements detected an increase in hydrophilicity due to the oxygenated functional groups and smoother surfaces as measured using XPS and AFM, respectively. Greater levels of hydrophilicity were observed for UV photooxidized than the ozonized PEN samples. The detection of grafted PAA on the surface of the treated PEN samples was difficult because of the ester groups in the bulk PEN. However, initial results showed a slight increase in hydrophilicity that can relate acrylic acid grafting onto ozone-treated PEN surfaces.

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**Surface modification of PEN treated with
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