Ring Opening of Aromatic Polymers by Remote Atmospheric-Pressure Plasma

Eleazar Gonzalez, II, Michael D. Barankin, Peter C. Guschl, and Robert F. Hicks

Abstract—An atmospheric-pressure oxygen and helium plasma was used to treat the surfaces of polyetheretherketone, polyphenylsulfone, polyethersulfone, and polysulfone. Water-contact-angle measurements, mechanical pull tests, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy were used to analyze the change in polymer properties. Plasma treatment converted all the materials from a hydrophobic to a hydrophilic state in a few tenths of a second. The adhesive bond strength was increased from 1.1 to 3.8 ± 1.0 MPa for polyetheretherketone and from 0.6 to 1.3 ± 0.2 MPa for polyphenylsulfone. XPS revealed that plasma treatment oxidizes between 7% and 27% of the aromatic carbon atoms on the polymer surfaces and converts them into aldehyde and carboxylic acid groups. The degree of oxidation was highest for polyetheretherketone, where the fraction of surface carbon atoms attributable to carbonyl (ketone and aldehyde) and carboxylic acid groups increased from 5% to 11% and from 0% to 19%, respectively. It is concluded that the O atoms generated in the atmospheric-pressure plasma oxidize and open the aromatic rings available on the polymer chains and that this is responsible for the increased adhesion.

Index Terms—Atmospheric plasma, bonding, plasma applications, plasmas, plastics, surface treatment.

I. INTRODUCTION

THERMOPLASTICS with aromatic polymer backbones are being increasingly used for structural components in aircraft, automobiles, electronics, and medical devices [1]–[6]. Polyetheretherketone (PEEK) is a desirable material for these applications because it has high thermal stability, excellent mechanical strength, and superior chemical properties [1]–[3]. A family of aromatic polymers containing sulfonated groups has also received much attention by the industry [4]–[15]. Included in this group are polysulfone (PSU), polyethersulfone (PES), and polyphenylsulfone (PPS). These polymers can be used continuously at temperatures up to 200 °C without any detrimental effect to their mechanical properties or chemical resistance [4]–[6], [14], [15]. The structure of the polymers is shown in Fig. 1. The rigid backbone, together with the diarylsulfone groups, stabilizes the S–C bonds and provides the desirable characteristics of these polymers [14].

Despite having attractive properties, a problem with some aromatic thermoplastics is their low surface energy, which can result in poor adhesion [1], [2], [5], [8]. In order to overcome this challenge, nonequilibrium plasmas have been used to modify the surfaces of these polymers without affecting their bulk properties [1], [3]–[6], [8], [10], [12], [14], [16]. Our group has treated polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) with a low-temperature atmospheric-pressure oxygen plasma [17]. It was found that the aromatic rings were attacked by oxygen atoms and possibly underwent ring opening and oxidation. In order to further test this hypothesis, we have examined the atmospheric plasma activation of PEEK, PPS, PES, and PSU. X-ray photoelectron spectroscopy (XPS) of these materials confirms that ring opening occurs with the formation of aldehyde and carboxylic acid groups on the polymer chains. The results of this study are reported hereinafter.

II. MATERIALS AND METHODS

A. Plasma Treatment

The plasma system used in these experiments has been described previously [17]. A 2-in linear plasma source was fed with 0.9 L/min of oxygen and 30.0 L/min of helium at 1 atm and an applied RF power of 200 W. A flow of 30.0 L/min of He was used because it produces a stable plasma. In addition, it has been found that the exit velocity of the gas from the
plasma source is approximately $2 \times 10^3$ cm/s, which gives optimal contacting of the polymer with the reactive species generated in the plasma. The oxygen flow rate was chosen by maximizing the amount of oxygen that would allow the plasma to remain stable. The source-to-substrate distance was 3 mm, and unless otherwise noted, a scan speed of 10 mm/s was used. Plasma exposure time was estimated using the same procedure as described previously [17]: The effective plasma beam width parallel to the scan direction was 2.1 cm. The exposure time equals the beam width divided by the scan speed and multiplied by the number of scans.

### B. Materials

Polyetheretherketone, polysulfone (Udel), and polyphenylsulfone (Radel R) with a thickness of 6.4 mm were obtained from Boedecker Plastics Inc. For XPS analysis, PEEK, PES, and PSU, approximately 0.1 mm thick, were obtained from CS Hyde Company, Inc. Large sheets of these polymers were cut into $3.8 \times 3.8$ cm$^2$ squares and cleaned with isopropyl alcohol. In order to remove any remaining solvent or water from the surface, the squares were then baked on a hot plate at 100°C.

### C. Surface Characterization

Water contact angles were recorded using a Krüss EasyDrop goniometer. Ten droplets, 0.2 μL in volume, were measured on each sample’s surface. For each sample, the mean and standard deviation were calculated. XPS was used to analyze the surface composition of the polymers before and after plasma treatment. Core-level photoemission spectra of the C 1s, O 1s, and S 2p lines were collected with a PHI 3057 spectrometer using Mg Kα X-rays at 1286.6 eV. All XPS spectra were taken in small area mode with a 7° acceptance angle and 23.5-eV pass energy. The detection angle with respect to the surface normal was 25°. All spectra were referenced to the C 1s peak of the graphitic carbon atom, with an assigned value of 285.0 eV. The surface atomic percentages were determined from the integrated intensity of the C 1s, O 1s, and S 2p photoemission peaks, divided by their sensitivity factors of 0.30, 0.71, and 0.67, respectively. Finally, surface roughness was measured using a VEECO DI3100 atomic force microscope. The root-mean-square surface roughness of the samples was obtained by using the software program Nanoscope V6.12r2.

### D. Adhesion Testing

The pull strengths of epoxy to polyetheretherketone, polysulfone, and polyphenylsulfone were measured using mechanical pull tests as described previously [17]. The adhesive was Hardman, Inc., epoxy (04004). The polymers were cut into $3.8 \times 3.8$ -cm$^2$ squares and plasma treated using 0.9-L/min O$_2$, 30.0-L/min He, 3-mm standoff distance, 200 W of RF power, 10-mm/s scan speed, and 4 total scans. The aluminum dollies were also scanned using the exact same conditions in order to increase adhesion to the dolly. The “control” sample was cleaned and bonded. The rest of the samples were scanned four times using the plasma parameters as previously mentioned. The “plasma” sample was immediately bonded after treatment. The “rinsed & aged” sample was rinsed with ethanol after treatment in order to remove any possible low-molecular-weight species [17]. This sample was dried with flowing nitrogen until ethanol was no longer visible on the surface and then allowed to continue drying for 90 min at 21°C, thus aging the sample, prior to adhesion. The “not rinsed & aged” sample was aged for 90 min at 21°C and then bonded.

### III. Results

Fig. 2 shows the effect of atmospheric plasma exposure time on the water contact angle of PEEK, PPS, PES, and PSU. The surface of each polymer was scanned once with the 2-in-wide plasma beam using scan speeds between 750 and 10 mm/s in order to vary the plasma exposure time. The other operating conditions are as described in the previous section. After a few tenths of a second of plasma exposure, the water contact angles drop to a constant low value that ranges between 24° for polysulfone and 12° for polyethersulfone. The fastest change obtained in water contact angle with time is for polyethersulfone, and the slowest is for polyetheretherketone.

The data in Fig. 2 follow an exponential decay function that is indicative of Langmuir adsorption kinetics [17]. The data
TABLE I
RATE PARAMETERS FOR THE EXPONENTIAL DECAY EQUATION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>WCA (0)</th>
<th>WCA (∞)</th>
<th>k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>80.6</td>
<td>18.1</td>
<td>8.4</td>
</tr>
<tr>
<td>PPS</td>
<td>79.9</td>
<td>19.6</td>
<td>24.8</td>
</tr>
<tr>
<td>PES</td>
<td>91.0</td>
<td>13.4</td>
<td>56.5</td>
</tr>
<tr>
<td>PSU</td>
<td>83.1</td>
<td>26.0</td>
<td>18.3</td>
</tr>
<tr>
<td>PET*</td>
<td>85.2</td>
<td>34.6</td>
<td>15.6</td>
</tr>
<tr>
<td>PEN*</td>
<td>85.2</td>
<td>21.7</td>
<td>4.6</td>
</tr>
</tbody>
</table>


were fitted as a function of exposure time $\tau$ with the following equation:

$$WCA(\tau) = WCA(\infty) + [WCA(0) - WCA(\infty)] \exp(-k\tau)$$

(1)

where $WCA(\infty)$ is the water contact angle after maximum plasma treatment, $WCA(0)$ is the initial water contact angle, and $k$ is the adsorption rate constant. The lines in the figure are the “best fits” of the equation to the data.

Table I lists the equation parameters for the “best fit” curves. The final water contact angles obtained are 26.0° for PSU, 19.6° for PPS, 18.1° for PEEK, and 13.4° for PES. In addition, the rate parameters for PET and PEN are included from previous work [17]. The rate constants range from 56.5 to 8.4 s⁻¹, and they increase in order PEEK < PSU < PPS < PES. In a previous study, the rate constants for PET and PEN were found to be 15.6 and 4.6 s⁻¹, respectively [17].

Fig. 3 shows the effect of plasma treatment on the pull strength for polymers adhesively bonded with epoxy. In addition, the pull strengths and failure modes for these samples are listed in Table II. All of the control samples fail at the adhesive/plastic interface. The plasma-treated PEEK samples fail at the adhesive/dolly interface and exhibit a fourfold increase in adhesion from 1.1 to 3.8 ± 0.9 MPa. Within experimental error, no difference is seen in adhesion for the rinsed or aged samples. Due to failure occurring at the adhesive/dolly interface, the strength of the bond may be underestimated by the pull test. The plasma-treated PPS samples exhibit an increase in adhesion from 0.6 to 1.3 ± 0.1 MPa. In this case, all the samples fail at the adhesive/plastic interface. Finally, within experimental error, no significant change is seen in adhesion between the control and the plasma-treated PSU samples, where pull strengths equal 3.3 ± 0.9 MPa.

Prior to XPS analysis, all samples were scanned four times using the same conditions as stated in the experimental methods section. The C 1s spectra of PEEK before and after plasma treatment are shown in Fig. 4. The C 1s spectrum for the original PEEK film was deconvoluted into three bands at 284.9, 286.4, and 287.2 eV, corresponding to carbon atoms in aromatic rings, carbon atoms with C–O single bonds, and carbon atoms with C = O double bonds (see inset diagram in Fig. 4) [18].
After plasma treatment, a new band in the C 1s spectrum of PEEK arises at 289.5 eV, which is attributed to carboxylic acid groups (COOH) [2], [17]. In addition, the relative amount of C = O groups on the surface increases significantly, while that of the C–O groups falls.

Table III lists the C 1s binding energies and surface composition of the PEEK before and after plasma treatment. Plasma oxidation causes the C:O ratio to drop from 5.6 to 2.0. For the untreated PEEK, the aromatic fraction of the carbon atoms (peaks 1 + 2) equals 95.2%, while the ketone fraction of the carbon atoms equals 4.8%. These percentages agree with the chemical formula for the polymer as well as with other XPS studies of PEEK [3], [18]. Plasma treatment results in the aromatic fraction decreasing to 70.1%, while that of the C = O species increases to 10.8%. The latter species are attributable to ketones and aldehydes. In addition, peak 4, which is not present in the control sample, accounts for 19.1% of the total C 1s spectrum. This latter peak is assigned to carboxylic acid functionality and results from aromatic ring opening and oxidation [2], [17].

The O 1s spectra of the control and plasma-treated PEEK are shown in Fig. 5. The O 1s spectra are composed of two peaks at 530.6 and 531.8 eV, corresponding to oxygen atoms with C = O double bonds and with C–O single bonds, respectively. The oxygen percentages are 33% for the former species and 67% for the latter species, as listed in Table IV. Plasma treatment causes the relative amount of the C = O groups to increase to 65.6%, while that of the C–O groups decreases to 34.4%. These results are expected, as the C 1s spectra of the plasma-treated PEEK show an increase in C = O and (C = O)−O bonds.

Fig. 5 shows the C 1s spectra of polyphenylsulfone before and after plasma exposure. The following peaks are observed for the control: 1) aromatic carbon atoms at 284.9 eV; 2) carbon associated with C–S bonds at 285.4 eV; and 3) carbon associated with C–O bonds at 286.4 eV (see inset diagram in Fig. 6) [6], [9], [11], [13]. After atmospheric plasma treatment, two new bands arise at 287.4 and 289.5 eV, corresponding to C = O and (C = O)−O functional groups, respectively [5], [6]. The C 1s spectra for untreated polyethersulfone and polysulfone exhibit the same peaks as those recorded for untreated
TABLE IV
OXYGEN 1S BINDING ENERGIES AND SURFACE COMPOSITION
OF THE POLYMERS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Binding Energy (eV)</th>
<th>C-O</th>
<th>S-O/C=O</th>
<th>S-O/C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>1</td>
<td>530.6</td>
<td>33.0%</td>
<td>65.6%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>531.8</td>
<td>67.0%</td>
<td>34.4%</td>
</tr>
<tr>
<td>PPS</td>
<td>1</td>
<td>531.9</td>
<td>50.2%</td>
<td>48.0%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>533.4</td>
<td>49.8%</td>
<td>52.0%</td>
</tr>
<tr>
<td>PES</td>
<td>1</td>
<td>531.9</td>
<td>66.6%</td>
<td>59.6%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>533.4</td>
<td>33.4%</td>
<td>40.4%</td>
</tr>
<tr>
<td>PSU</td>
<td>1</td>
<td>531.9</td>
<td>52.3%</td>
<td>46.7%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>533.4</td>
<td>47.7%</td>
<td>53.3%</td>
</tr>
</tbody>
</table>

Fig. 6. Carbon 1s XPS spectra of (a) control PPS and (b) plasma-treated PPS.

Fig. 7. Oxygen 1s XPS spectra of (a) control PPS and (b) plasma-treated PPS.

Fig. 8. Sulfur 2p XPS spectra of (a) control PPS and (b) plasma-treated PPS.

Moreover, both of these polymers show the two new C 1s peaks at high binding energy following plasma treatment.

The C 1s binding energies and surface composition of PPS, PES, and PSU are presented in Table III. All three of the sulfonated polymers yield similar results when exposed to the atmospheric plasma. The C:O ratio of PPS drops from 5.1 to 1.8, while that of PES falls from 5.2 to 2.1 and that of PSU falls from 6.0 to 2.3. The aromatic fraction of the carbon atoms (peaks 1 + 2 + 3) in PPS, PES, and PSU initially equals 100%. After plasma treatment, the aromatic fraction decreases to 86.0%, 89.9%, and 90.7%, respectively. Most significantly, atmospheric plasma oxidation produces aldehyde and carboxylic acid groups on all three sulfonated polymers. The percentages of these two groups are about equal, accounting for 14%, 10.1%, and 9.3% of the surface carbon on the treated PPS, PES, and PSU, respectively. Note that for PSU, the three aliphatic carbons present in the polymer chain have been lumped into the aromatic fraction.

Fig. 7 shows the O 1s spectra of polyphenylsulfone before and after exposure to the plasma. The spectra are deconvoluted into two bands. For the control, the first peak at 531.9 eV is attributed to S = O bonds, while the second peak at 533.4 eV is assigned to C–O groups. After plasma treatment, peak 1 is assigned to oxygen atoms with S = O and C = O double bonds, since the O 1s binding energies for these species are identical.
TABLE V
SULFUR 2P BINDING ENERGIES AND SURFACE COMPOSITION
OF THE POLYMERS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Peak #</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Control</th>
<th>Fraction of total Sulfur (%)</th>
<th>Plasma</th>
<th>Fraction of total Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS</td>
<td>1</td>
<td>167.5</td>
<td>O=S=O</td>
<td>100.0%</td>
<td>65.8%</td>
<td>2</td>
<td>168.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>168.5</td>
<td>SO$_2^-$</td>
<td>0.0%</td>
<td>34.2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>1</td>
<td>167.5</td>
<td>O=S=O</td>
<td>100.0%</td>
<td>66.6%</td>
<td>2</td>
<td>168.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>168.5</td>
<td>SO$_2^-$</td>
<td>0.0%</td>
<td>33.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSU</td>
<td>1</td>
<td>167.5</td>
<td>O=S=O</td>
<td>100.0%</td>
<td>63.7%</td>
<td>2</td>
<td>168.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>168.5</td>
<td>SO$_2^-$</td>
<td>0.0%</td>
<td>36.3%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[12]. Both polyethersulfone and polysulfone are deconvoluted in the same manner. The O 1s binding energies and surface composition of PPS, PES, and PSU are presented in Table IV. Plasma activation causes peak 1 to decrease by 2.2%, 7.0%, and 5.6% for PPS, PES, and PSU, respectively, while peak 2 increases by the same amount for each polymer.

The sulfur 2p spectra of polyphenylsulfone are shown in Fig. 8. The control spectrum shows a doublet with binding energies of 167.5 eV (2p$_{1/2}$) and 168.9 eV (2p$_{3/2}$) [4]. These peaks are due to the sulfone species. After plasma treatment, a new doublet is observed with binding energies of 166.9 and 169.9 eV. These bands are most likely due to sulphate species (SO$_4^{2-}$) [4]. These data indicate that a portion of the sulfur groups are oxidized by the plasma. Table V shows the sulfur 2p binding energies of PPS, PES, and PSU before and after plasma treatment. All three polymers exhibit the same results. Plasma treatment converts approximately 34% of the surface sulfone groups into sulphate groups.

IV. DISCUSSION

The change in water contact angle with plasma exposure time follows an exponential decay function as predicted for Langmuir adsorption kinetics [see (1)] [17]. The adsorption rate constants ($k$) range from 8.4 s$^{-1}$ for PEEK to 56.5 s$^{-1}$ for PES as shown in Table I. These values may be compared to the rate constants recorded previously for polyethylene terephthalate and polyethylene naphthalate, which equal 15.6 and 4.6 s$^{-1}$, respectively [17].

We propose that the primary species attacking the polymer chains are O atoms. The concentration of O atoms in the exit beam of the plasma source is $\sim 10^{16}$ cm$^{-3}$, as determined previously by numerical modeling of the reaction kinetics and by titration of the O atoms with NO [27]. The rate of the adsorption of oxygen atoms is given by

$$R_a = 1/4 \, \nu S_0 C_O (1 - \theta_s)$$  \hspace{1cm} (2)

where $\nu$ is the mean molecular speed of the oxygen atoms in the gas (in centimeters per second), $S_0$ is the zero coverage sticking probability, $C_O$ is the concentration of oxygen atoms in the gas above the surface (in moles per cubic centimeter), and $\theta_s$ is the fraction of sites that have been attacked by the oxygen atoms. The adsorption rate constant $k$ is equal to $R_a$ divided by $(1 - \theta_s) \cdot [L_s]$, where $[L_s]$ is the density of reactive sites on the polymer surface (in moles per square centimeter). Solving for $k$ from (2) yields

$$k = 1/4 \, \nu S_0 C_O / [L_s].$$  \hspace{1cm} (3)

Given that the plasma exposure conditions are the same in each experiment, then the difference in the rate constants observed for each polymer should be due to changes in either the sticking probability, the density of reactive sites, or both. It may be postulated that the density of reactive sites is proportional to the number of aromatic rings per monomer unit, provided that all the functional groups on the polymer chain are the same. If this is the case, then one would expect the rate constant of PEN to be half that of PET, and the rate constants of PSU and PPS to equal one another and be half that of PES. Examination of the data in Table I shows that the rate constants do follow these trends. Furthermore, the fact that the rate constants are all in the same range, between 5 and 50 s$^{-1}$, suggests that the reactive sticking probabilities are close to one another for this family of aromatic polymers.

It is well known that plasma treatment can improve the adhesive bond strength in cases where the polymer exhibits poor adhesion to glue [17], [19]–[21]. In this paper, it was found that exposure to the atmospheric-pressure helium and oxygen plasma increased the bond strength of PEEK to epoxy by 3.5 times and of PPS to epoxy by 2.0 times, but had no effect on PSU. In the latter case, this is due to the surface of PSU already being activated enough that treatment by plasma does not increase adhesion. The adhesively bonded control sample for PSU has a pull strength of 3 MPa, approximately three times higher than that of the PEEK and the PSU control samples. It should be noted that the particular combination of adhesive and polymer determines whether or not plasma treatment will enhance bond strength. For example, we have found that plasma treatment of polymethyl methacrylate can improve adhesion to epoxy and silicone adhesives, but no change is seen for urethane or acrylate glues [28].

The 3.5 jump in adhesion seen for PEEK is comparable to that reported in the literature. Hicks et al. [22] observed a significant increase in the lap shear strength of epoxy-bonded PEEK composites after exposure to the atmospheric-pressure helium and oxygen plasma. Comyn et al. [23], [24] were able to double the bond strength of PEEK to an epoxy adhesive film using a vacuum oxygen plasma and a corona discharge. To our knowledge, no previous studies have been made on surface activation and bonding of PPS. Note that no difference in adhesion was seen for samples that were rinsed with ethanol or aged for 90 min at room temperature. In addition, AFM of PEEK was examined, and no significant change was observed in the surface morphology upon plasma treatment, consistent with previous studies [22], [23].

The changes observed in water contact angle and adhesion result from the creation of new functional groups on the polymer surfaces. Analysis of the plasma-treated PEEK by XPS showed that the fraction of aromatic carbon atoms on the surface decreased from 95.2% to 70.0%, while the amount of carbonyl (ketone and aldehyde) and carboxylic acid

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groups increased from 4.8% to 10.8% and from 0.0% to 19.1%, respectively. According to Inagaki et al. [3], the interaction of an oxygen plasma with PEEK will result in cleavage of the C–O bond at the phenyl-ether site and the C–C bond at the benzophenone site, since these are the weakest bonds in the polymer chain. This allows for the insertion of oxygen along the polymer backbone. The only way to introduce \( \text{C} = \text{O} \) functional groups without opening the aromatic ring is to add oxygen to the ketone group after bond scission. The ratio of ketone carbon atoms to aromatic carbon atoms in the chemical structure of PEEK is 1:19 (~5%). If this were the sole location of newly created \( \text{C} = \text{O} \) groups, then at most 5% of the carbon would be associated with these species after plasma treatment. By contrast, our data show that there is four times this amount. Therefore, we conclude that the aromatic rings are attacked directly by the oxygen atoms in the plasma afterglow and undergo ring opening with the formation of aldehydes and carboxylic acids.

According to the XPS data, oxygen plasma treatment of PES causes roughly 10% of the aromatic carbon atoms to be converted into equal amounts of aldehyde and carboxylic acid groups. Other researchers have detected “ester-like” groups on the surface of PES after exposing it to an oxygen plasma in vacuum [4], [5], [8]. Because all the carbon atoms on the surface of PES are present in aromatic form, the C = O and \( (\text{C} = \text{O})–\text{O} \) species must arise from ring opening. Feng et al. [4] also suggest that ring opening occurs on the surface of PES. Analysis of PPS and PSU leads to the same conclusion, i.e., that about 10% of the aromatic carbons atoms are converted into aldehyde and carboxylic acid groups by exposure to the atmospheric-pressure oxygen plasma.

A proposed mechanism for the atmospheric plasma oxidation of polyethersulfone is shown in Fig. 9. The same mechanism should be operative for all four aromatic polymers. In the first step, ground-state oxygen atoms insert into the aromatic double bond, forming a three-member epoxy ring. This is analogous to the mechanism observed for the oxidation of graphite [29]–[32]. In step (2), the strain in the epoxy group is relieved by breaking the C–C bond and forming a seven-member ring [29], [30]. Step (3) consists of a resonance-stabilized rearrangement of electrons with ring opening and the generation of an aldehyde on one end of the chain and a highly reactive carbene group on the other end. In step (4), another aldehyde is created by addition of an O atom to the carbene. In the last step, a third O atom attacks the aldehyde and inserts across the C–H bond to form the carboxylic acid. The mechanism proposed in Fig. 9 is consistent with the organic chemistry literature, with the XPS results, and with the high concentration of ground-state O atoms in the afterglow of the atmospheric-pressure radio-frequency plasma.

V. CONCLUSION

The surfaces of polyetheretherketone, polyphenylsulfone, polyethersulfone, and polysulfone were activated using an atmospheric-pressure helium and oxygen plasma. The pull strength for plasma-treated PEEK and PPS increased 3.5 and 2.0 times, respectively, while no increase was seen for PSU. The increase in adhesion may be attributed to oxygen atom attack of the aromatic groups with ring opening and oxidation to form aldehydes and carboxylic acids on the polymer surfaces.
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