# Defining the Surface Chemistry of Ammonia-Modified Poly(tetrafluoroethylene-*co*-hexafluoropropylene) Films

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ABSTRACT: Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film samples were surface-modified by exposure to a UV-activated mercury/ammonia environment (called the "mercat reaction"), yielding a hydrophilic surface with a diversity of functional groups. We describe herein the functionality of mercatmodified FEP and ultimately hope to use these defined surfaces in biomedical applications, specifically to enhance the interaction of cells at the FEP interface. Following the mercat reaction, advancing and receding water contact angles decreased from 120°/101° for FEP to 71°/27° for mercat-modified FEP. By comparison to small molecule chemistry, we had expected the film samples to have imine and nitrile functional groups; however, XPS analysis of mercat-modified film samples indicated the presence of both nitrogen and oxygen functional groups. From a series of labeling reactions, the surface functional groups were found to include nitrile, amine, carboxylic acid, hydroxyl, and carbon–carbon double bonds. Hydrolysis of nitrile functional groups resulted in an increased carboxylic acid concentration from 10% to 38% and decreased water contact angles from 71°/27° to 61°/30°. Bromination/amination of carbon– carbon double bonds resulted in an increased amine concentration from 8% to 10% and decreased water contact angles from 71°/27°. To 54°/24°. Future studies will correlate surface chemistry of these defined mercat-modified FEP film samples with neuronal cellular response.

### Introduction

Surface chemistry and topography define a material's interfacial properties, influencing the way in which a material interacts with others. Since cells are known to respond to both surface chemistry and morphology,<sup>1,2</sup> we are particularly interested in modifying surface chemistry without affecting surface roughness. By controlling surface chemistry alone, we aim to correlate a specific functionality with a cellular response.

Polymer surface modification has been studied for numerous years, and several techniques have been used to change the interfacial properties while maintaining those of the bulk.<sup>3</sup> Fluoropolymers are particularly advantageous, allowing discrete interfaces to be prepared with specific functionality, such as carboxylic acid, hydroxyl, amine, etc.<sup>4</sup> Small molecule organic chemistry can be used to prepare well-defined fluoropolymer surface chemistries yet require highly reactive species to effect a reaction.<sup>5,6</sup> Defined plasma systems can also be used to modify surfaces yet often result in the introduction of multiple functional groups.<sup>7,8</sup> Recently, we demonstrated that fluoropolymer films could be modified in a UV-activated mercury-ammonia environment (called the mercat reaction) to introduce imine functionality.<sup>9</sup> The modified surface, while not as functionally uniform as those prepared by chemical modification, was relatively easy to prepare, hydrophilic, and topographically smooth.

We describe herein the chemical functional groups of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film surfaces prepared by the mercat reaction which has been used for small molecules and poly(tetrafluoroethylene).<sup>10</sup> According to published literature for small



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**Figure 1.** Proposed mechanism for the introduction of reactive functional groups to the surface of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) by a mercury/ammonia UVphotosensitization reaction<sup>10</sup> to yield FEP–[N/O].

molecules,<sup>10</sup> and as shown in Figure 1 for FEP, we anticipated that nitrile and imine functional groups would be introduced to the FEP surface. We took advantage of the presence of these functional groups, oxidizing the nitrile to carboxylic acid and brominating/ aminating the imine carbon–carbon double bonds to amine. These series of reactions allowed us to increase the number of reactive functional groups available for further modification with, for example, cell adhesive peptides. While the mechanism does not account for oxygen functionality, we found that mercat-modified FEP film surfaces (FEP–[N]/[O]) were complicated, containing both nitrogen and oxygen functionalities. We



**Figure 2.** FEP–[N/O] film surfaces were labeled to determine the relative concentrations of reactive functional groups and then further modified to increase the surface concentration of carboxylic acid and amine functional groups.

gained insight into the types of functional groups present from a series of labeling reactions that we analyzed by X-ray photoelectron spectroscopy (XPS) and dynamic water contact angles. Figure 2 summarizes the series of reactions that were carried out on FEP–[N/O] film samples.

# **Experimental Section**

All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received unless otherwise indicated. Tetrahydro-furan (THF, Fisher, Nepean, ON) was distilled from sodium benzophenone dianion and stored under nitrogen. FEP films (5 mil thickness, received from DuPont and cut into 4 cm  $\times$  2

Table 1. Introduction and Labeling of Reactive Functional Groups of $FEP- N ^{2}$	Table 1	I. Introduction	and Labeling	of Reactive	Functional	<b>Groups</b> o	f FEP-	[N/C	וו
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film sample	С	F	0	Ν	Cl/Tl	$\theta_{\rm A}$ (deg)	$\theta_{\mathrm{R}}$ (deg)
FEP	31.1	68.9				$120\pm2$	$101\pm2$
FEP-[N/O]	70.8	5.6	9.2	14.3		$71\pm3$	$27\pm2$
FEP-[O]-N-CH-C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub>	68.4	10.7	13.0	6.9	1.0	$64\pm2$	$24\pm 1$
FEP-NH-CO-CCl <sub>3</sub> /O-CO-CCl <sub>3</sub>	68.8	3.6	11.5	9.5	6.6	$73\pm1$	$34\pm2$
FEP-N-CH-C <sub>6</sub> F <sub>5</sub> /O-CO-CCl <sub>3</sub>	57.6	12.1	18.9	6.6	4.8	$69\pm2$	$30\pm3$
FEP-[N]/COOTl	76.8	3.5	9.5	9.7	0.5	$71\pm 1$	$29\pm2$

cm samples) were Soxhlet-extracted in THF for 24 h. All water was deionized and distilled from Millipore Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 M $\Omega$  resistance. All reactions were carried out in a dry, inert argon atmosphere unless otherwise specified. All reagents were transferred by either cannula or syringe.

XPS data were collected on a Leybold LH Max 200 using a Mg Ka X-ray source at 15 kV and 20 mA emission current. An aperture size of 13  $\times$  7  $\mu m$  was used to collect data at takeoff angles of 20° and 90° between sample and detector (n = 3 samples). Unless otherwise specified, all of the data presented were taken at a 20° takeoff angle. Advancing and receding water contact angles were obtained on a Ramé-Hart NRL telescopic goniometer using a Gilmont syringe with a 22 gauge flat-tipped needle. Values reported represent the average and standard deviation of five measurements per sample (n = 3 samples). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained on a Mattson Galaxy 5400 spectrometer using a germanium crystal (45°). Scanning electron microscopy (SEM) micrographs of samples coated with gold for 15 s were taken on a Hitachi S4500 field emission microscope at 5 kV acceleration voltage.

**Introduction of Functional Groups to FEP (FEP–[N/O]).** FEP–[N/O] film samples were prepared as previously described.<sup>9,10</sup> Briefly, a quartz Schlenk tube, containing FEP film samples and a drop of mercury, was evacuated (P < 0.01 mmHg) and purged with argon (three times). After the fourth evacuation, the tube was refilled with gaseous ammonia (99.99% purity, BOC, Etobicoke, ON) to 1 atm pressure. The tube was placed in a UV reactor (Rayonet, Branford, CT), and the films were irradiated at 254 nm with eight 15 W mercury lamps for 24 h.

Labeling the Amine Groups of FEP–[N/O] with 2,3,5-Trichlorobenzaldehyde (FEP–[O]/N–CH–C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>). FEP– [N/O] film samples were immersed in 20 mL of a 0.012 M 2,3,5trichlorobenzaldehyde solution in THF containing 1 mL of pyridine for 24 h at room temperature (RT). Film samples were then rinsed three times each in THF, methanol, and then dichloromethane prior to drying under vacuum (P < 0.01mmHg). Unmodified FEP film samples were treated identically, thereby serving as controls.

Labeling the Amine and Hydroxyl Groups of FEP– [N/O] with Trichloroacetyl Chloride (FEP–NH–CO– CCl<sub>3</sub>/O–CO–CCl<sub>3</sub>). FEP–[N/O] film samples were immersed in 20 mL of a 9 × 10<sup>-5</sup> M trichloroacetyl chloride solution in THF containing 1 mL of pyridine for 24 h at RT. Film samples were rinsed three times each in THF, methanol, and then dichloromethane prior to drying under vacuum (P < 0.01mmHg). Unmodified FEP film samples were treated identically, thereby serving as controls.

Labeling the Amine Group of FEP–[N/O] with Pentafluorobenzaldehyde and Then the Hydroxyl Group of FEP–[N/O] with Trichloroacetyl Chloride (FEP–N– CH–C<sub>6</sub>F<sub>5</sub>/O–CO–CCl<sub>3</sub>). FEP–[N/O] film samples were immersed in 20 mL of a 5 × 10<sup>-5</sup> M pentafluorobenzaldehyde solution in THF with 1 mL of pyridine for 24 h at RT. FEP– N–CH–C<sub>6</sub>F<sub>5</sub> film samples were then immersed in 20 mL of a 9 × 10<sup>-5</sup> M trichloroacetyl chloride solution in THF with 1 mL of pyridine for 24 h at RT. The film samples were rinsed three times each in THF, methanol, and then dichloromethane prior to drying under vacuum (P < 0.01 mmHg). Unmodified FEP film samples were treated identically, thereby serving as controls.

Labeling the Carboxylic Acid Groups of FEP-[N/O] with Thallous Ethoxide (FEP-[N]/COOTI).<sup>11</sup> FEP-[N/O] film samples were immersed in 10 mL of thallous ethoxide for 60 s at RT and then rinsed six times with ethanol prior to drying under vacuum (P < 0.01 mmHg). Unmodified FEP film samples were treated identically, thereby serving as controls.

**Hydrolysis of the Nitrile Groups of FEP–**[**N**/**O**] (**FEP–COOH**).<sup>12</sup> FEP–[**N**/**O**] film samples were immersed in 10 mL of concentrated HCl for 48 h at RT and then washed five times with water. Subsequently, the film samples were immersed in 10 mL of a 10 M NaOH solution for 48 h at RT and then rinsed five times each in water, 5% of a 10 M oxalic acid solution, water, and then 95% ethanol prior to drying under vacuum (P < 0.01 mmHg). FEP–COOH film samples were labeled with thallous ethoxide (FEP–COOTI) as described above for FEP–[**N**/**O**] film samples, with the latter serving as controls for the labeling of FEP–COOH.

**Bromination of the Carbon–Carbon Double Bonds of FEP–[N/O] (FEP–[N/O]–Br).**<sup>13</sup> FEP–[N/O] film samples were immersed in 20 mL of a 0.2 M bromine solution in dichloromethane for 24 h at 0 °C in the dark. The film samples were then sequentially rinsed five times each with dichloromethane, methanol, and THF and dried under vacuum (P < 0.01 mmHg).

**Amination of Brominated FEP–[N/O]–Br (FEP–NH<sub>2</sub>).** A 10 mL aliquot of ammonia was condensed onto sodium at –78 °C and then distilled into a Schlenk tube containing FEP– [N/O]–Br film samples that were equilibrated at –196 °C. The tube was allowed to warm to RT, and the reaction proceeded for 24 h after which the film samples were sequentially washed three times each with methanol, dichloromethane, and THF prior to drying under vacuum (P < 0.01 mmHg). FEP–NH<sub>2</sub> film samples were labeled with 2,3,5-trichlorobenzaldehyde (FEP–N–CH–C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>) and trichloroacetyl chloride (FEP–NH–CO–CCl<sub>3</sub>) as previously described for FEP–[N/O] film samples, with the latter serving as controls for the labeling of FEP–NH<sub>2</sub>.

### **Results and Discussion**

**Introduction of Surface Functional Groups to** FEP (FEP-[N/O]). FEP film samples were modified by the mercat reaction to introduce surface reactive functional groups. Since we previously showed that FEP films modified by the mercat reaction for 3, 24, and 72 h showed similar properties after 24 h,9 all of the reactions described herein were based on 24 h modified film surfaces. As was shown in Figure 1 (and as adapted from Burdeniuc et al.<sup>10</sup>), the activated mercury-ammonia system led to the introduction of nitrile and imine functional groups. However, as shown in Table 1, the XPS data indicated the presence of both nitrogen and oxygen functional groups in the FEP-[N/O] film samples, thereby indicating a more complex surface chemistry than that accounted for by the proposed reaction scheme. The oxygen functional groups may have resulted from (1) air oxidation of nitrile or unsaturated carbon-carbon double bonds and/or (2) a nonspecific reaction during (or after) the mercat reaction between the UV-activated surface and trace oxygen or water. After the 24 h mercat reaction, the surface was defluorinated while nitrogen, oxygen, and carbon atomic concentrations increased (C70.8F5.6O9.2N14.3). Consequently, both the advancing and receding contact angles decreased from 120°/101° to 71°/27°, reflecting the

Table 2. Hydrolysis of Nitrile Groups of FEP-[N/O] and Labeling of Carboxylic Acid Groups with Thallous Ethoxide

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film sample	С	F	0	Ν	Cl/Tl	$\theta_{\rm A}$ (deg)	$\theta_{\mathrm{R}}$ (deg)
FEP-[N/O]	70.8	5.6	9.2	14.3		$71\pm3$	$27\pm2$
FEP-COOH	71.1	9.8	13.7	5.3		$61\pm3$	$30\pm2$
FEP-COOT1	52.9	21.7	18.7	3.2	3.5	$75\pm1$	$47\pm1$
FEP-[N/O] + EtOTl (control)	76.8	3.5	9.5	9.7	0.5	$71\pm 1$	$29\pm2$

 Table 3. Bromination/Amination of Carbon-Carbon Double Bonds of FEP-[N/O] and Labeling of Amine Groups with

 Either 2,3,5-Trichlorobenzaldehyde or Trichloroacetyl Chloride

film sample	С	F	0	Ν	Cl/Tl	$\theta_{\rm A}$ (deg)	$\theta_{\rm R}$ (deg)
$FEP-[N/O]$ $FEP-[N/O]-Br$ $FEP-NH_2$ $FEP-N-CH-C_6H_2C]_2$	70.8 67.7 69.4 71.3	5.6 2.9 2.9 1.9	9.2 11.3 16.0 18.4	14.3 9.4 11.7 6.9	8.7 1.5	$71 \pm 3 \\ 60 \pm 3 \\ 54 \pm 3 \\ 75 \pm 1$	$27 \pm 2 \\ 33 \pm 1 \\ 24 \pm 2 \\ 30 \pm 2$
$\begin{array}{l} \mbox{FEP}-[N/O] + OHC-C_6H_2Cl_3 \mbox{ (control)} \\ \mbox{FEP}-NH-COCCl_3 \\ \mbox{FEP}-[N/O] + CICOCCl_3 \mbox{ (control)} \end{array}$	68.4 67.8 68.8	10.7 3.6 3.6	13.0 10.2 11.5	6.9 9.1 9.5	1.0 9.3 6.6	$64 \pm 2 \\ 69 \pm 2 \\ 73 \pm 1$	$egin{array}{c} 24\pm1\\ 23\pm1\\ 34\pm2 \end{array}$

increased hydrophilic nature of FEP–[N/O] film samples. SEM micrographs of FEP and FEP–[N/O] film samples were identical and smooth, having no topographical features. Thus, the large hysteresis between advancing and receding contact angles likely reflected the chemical heterogeneity of FEP–[N/O] film samples as opposed to surface roughness. The ATR–FTIR spectrum of FEP had the characteristic fluoropolymer peaks with  $\nu_{C-F}$  at 1210 and 1153 cm<sup>-1</sup>. After the mercat reaction, additional small peaks were observed for  $\nu_{N-H}$  at 3500 cm<sup>-1</sup>,  $\nu_{C=0}$  at 1780 cm<sup>-1</sup>, and  $\nu_{C=N}$  at 2420 cm<sup>-1</sup>.

Identifying the Surface Functional Groups of FEP–[N/O]. To understand the complex surface chemistry resulting from the mercat reaction, the available functional groups were labeled or further modified, as was shown in Figure 2. The XPS and contact angle data for the labeling reactions were reproducible and are summarized in Table 1. Amine functional groups present on the FEP–[N/O] film samples were labeled with 2,3,5-trichlorobenzaldehyde to yield FEP–[O]/N–CH–C<sub>6</sub>H<sub>2</sub>-Cl<sub>3</sub> (C<sub>68.4</sub>F<sub>10.7</sub>O<sub>13.0</sub>N<sub>6.9</sub>Cl<sub>1.0</sub>). The presence of chlorine, as detected by XPS, indicated the success of this reaction. While the decrease in nitrogen atomic concentration may be explained by the presence of the bulky phenyl ring, the increase in fluorine atomic concentration may suggest slight surface erosion following modification.

Available amine and hydroxyl functional groups on FEP-[N/O] were labeled with trichloroacetyl chloride, as evidenced by the presence of chlorine in the XPS data, to yield FEP-NH-CO-CCl<sub>3</sub>/O-CO-CCl<sub>3</sub> (C<sub>68.8</sub>- $F_{3.6}O_{11.5}N_{9.5}Cl_{6.6}$ ). The increase in oxygen and decrease in nitrogen and fluorine concentrations relative to FEP-[N/O] further confirmed the success of this reaction. As might be expected, the receding contact angle increased slightly, reflecting the relative hydrophobic nature of the ester and amide (73°/34°) of FEP-NH-CO-CCl<sub>3</sub>/  $O-CO-CCl_3$  to the hydroxyl and amine (71°/27°) of FEP-[N/O]. As a further gauge of the relative concentration of oxygen functionality present as hydroxyl, the amine groups were blocked by reaction with pentafluorobenzaldehyde, leaving only hydroxyl groups available for reaction with trichloroacetyl chloride. As expected, the resulting films,  $FEP-N-CH-C_6F_5/O-CO-CCl_3$ (C57.6F12.1O18.9N6.6Cl4.8), had an XPS chlorine concentration less than FEP-N-CO-CCl<sub>3</sub>/O-CO-CCl<sub>3</sub> film samples, indicating the success of these reactions. The increased fluorine and oxygen atomic concentrations in FEP-N-CH-C<sub>6</sub>F<sub>5</sub>/OCO-CCl<sub>3</sub> further confirmed this success.

Using the XPS data, the relative concentrations of surface functional groups were calculated assuming that<sup>14,15</sup> (i) trichloroacetyl chloride reacted with all available hydroxyl and amine groups, (ii) trichlorobenzaldehyde and pentafluorobenzaldehye reacted only and with all available amine groups, and (iii) the labeling reactions were quantitative. For FEP–[N/O], 8–15% of the surface oxygen concentration was attributed to hydroxyl functional groups and 5–12% of the surface nitrogen concentration was attributed to amine functional groups.

To determine whether any of the remaining oxygen concentration could be attributed to carboxylic acid functional groups, FEP–[N/O] surfaces were labeled with thallous ethoxide. Assuming quantitative yields, we calculated that 10% of the surface oxygen existed as carboxylic acid groups on FEP–[N]/COOTI film surfaces. Since we are interested in using the FEP–[N/O] surfaces for further modification with peptides, we did not explore the range of additional possible oxygen functional groups present; however, we were interested in determining whether the functional groups proposed in Figure 1 could be exploited to provide a surface with an increased number of functional groups for modification.

**Increasing the Functionality of FEP–[N/O]: Hydrolysis and Bromination/Amination.** As was described in the proposed mechanism for mercat-modified FEP films (cf. Figure 1), FEP–[N/O] films contained both nitrile and imine functional groups. To both confirm the presence of these functional groups while at the same time increasing the number of reactive handles available for further modification with peptides, nitrile groups were hydrolyzed to carboxylic acids and carbon–carbon double bonds were brominated and then aminated to amines (cf. Figure 2). The XPS and contact angle data are summarized in Tables 2 and 3.

The nitrile groups of FEP-[N/O] film samples were hydrolyzed by strong acid and strong base to carboxylic acids, yielding FEP-COOH (C71.1F9.8O13.7N5.3). As shown in Table 2, relative to FEP-[N/O], the XPS atomic concentration of nitrogen decreased while oxygen increased, indicating the success of this reaction. In addition, the advancing contact angle decreased, reflecting the increased hydrophilicity of carboxylic acidmodified surfaces  $(61^{\circ}/30^{\circ})$  over those with nitrile groups. To further confirm the conversion of nitriles to carboxylic acids, FEP-COOH films were labeled with thallous ethoxide, yielding FEP-COOTl, and compared to FEP-[N/O] films labeled similarly (FEP-[N]-COOTI). As expected, the XPS concentration of thallium on FEP-COOTl (C<sub>63.6</sub>F<sub>12.3</sub>O<sub>17.2</sub>N<sub>3.4</sub>Tl<sub>3.5</sub>) films was much greater than controls (FEP-[N]-COOTl). From the XPS

data, and assuming that all nitrile groups were hydrolyzed to carboxylic acids, the relative percent of oxygen functionality attributed to carboxylic acid groups was calculated to increase from 10% for FEP-[N/O] to 38% for FEP-COOH. On the basis of these data, 70% of the surface nitrogen concentration was attributed to nitrile functional groups.

The carbon-carbon double bonds of FEP-[N/O] film samples were brominated by the reaction with bromine dissolved in dichloromethane to FEP-[N/O]-Br (C<sub>67.7</sub>- $F_{2.9}O_{11.3}N_{9.4}Br_{8.7}$ ) and then aminated by the reaction with ammonia to  $FEP-NH_2$  ( $C_{69.4}F_{2.9}O_{16.0}N_{11.7}$ ). Following the success of the bromination/amination reactions was facilitated by first the presence and then the absence of bromine in the XPS spectrum. Compared to brominated films, aminated films also had a higher concentration of nitrogen. On the basis of XPS data, the concentration of carbon present as carbon-carbon double bonds was estimated at 6%. As may be expected, the advancing contact angle decreased following bromination  $(60^{\circ}/33^{\circ})$  and then further decreased following amination  $(54^{\circ}/24^{\circ})$ .

To confirm that FEP-NH<sub>2</sub> film samples had more amine groups than FEP-[N/O] control film samples, both were labeled with either 2,3,5-trichlorobenzaldehyde or trichloroacetyl chloride. As shown in Table 3 for the reaction with 2,3,5-trichlorobenzaldehyde, FEP-N-CH-C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub> (C<sub>71.3</sub>F<sub>1.9</sub>O<sub>18.4</sub>N<sub>6.9</sub>Cl<sub>1.5</sub>) had slightly more chlorine and carbon and less fluorine than control film samples. In addition, the contact angles of FEP-N- $CH-C_6H_2Cl_3$  increased (75°/30°) relative to FEP-NH<sub>2</sub>, reflecting the increased hydrophobicity of benzaldehydelabeled amines vs unlabeled amines (54°/24°). For the reaction with trichloroacetyl chloride, FEP-NH-CO-CCl<sub>3</sub> film samples (C<sub>67.8</sub>F<sub>3.6</sub>O<sub>10.2</sub>N<sub>9.1</sub>Cl<sub>9.3</sub>) had a greater concentration of chlorine than FEP-[N/O] control film samples labeled similarly, thereby further confirming the increase in amine functional groups of FEP-NH<sub>2</sub> vs FEP-[N/O]. Relative to brominated/aminated FEP-NH<sub>2</sub> film samples, trichloroacetyl chloride-labeled FEP-NH–COCCl<sub>3</sub> film samples had a higher advancing contact angle (69°/23°), indicating a more hydrophobic surface, as may be expected. Assuming that the concentration of hydroxyl groups was unaffected by the bromination/amination reactions, we calculated that the number of surface amine groups increased from  $\sim 8\%$ for FEP-[N/O] to  $\sim 10\%$  for FEP-NH<sub>2</sub> on the basis of the XPS data.

# **Conclusions**

FEP film surfaces were modified by the facile mercat reaction introducing predominantly nitrile, imine, carboxylic acid, and hydroxyl functional groups. We used a series of labeling reactions to determine the relative percentages of reactive functional groups and modified the existing functional groups to increase the surface chemical reactivity. These reactions indicated that, of the nitrogen functional groups, 8% were attributed to amine and 70% to nitrile. On the basis of similar calculations of the oxygen functional groups, 8-15% were attributed to hydroxyl and 10% to carboxylic acid. Hydrolysis of the nitrile functional groups present on FEP-[N/O] surfaces resulted in an increased carboxylic acid concentration, accounting for 38% of the available oxygen. Bromination/amination of the imine carboncarbon double bonds of FEP-[N/O] resulted in increased amine concentration, accounting for  $\sim 10\%$  of the surface nitrogen functional groups. Relative to FEP-[N/O] film samples, both FEP–COOH and FEP–NH<sub>2</sub> film samples had higher concentrations of surface reactive functional groups available for further modification.

Future studies will take advantage of the increased reactivity of the FEP-COOH and FEP-NH<sub>2</sub> film surfaces by covalently bonding cell adhesive peptides derived from laminin. The peptide-modified films will be used in model systems of nerve regeneration to study the interaction of primary neurons of the central nervous system.

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