Generation of functional PET microfibers through surface-initiated polymerization

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In this study, we report on a facile and robust method by which poly(ethylene terephthalate) (PET) surfaces can be chemically modified with functional polymer brushes while avoiding chemical degradation. The surface of electrospun PET microfibers has been functionalized by growing poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) brushes through a multi-step chemical sequence that ensures retention of mechanically robust microfibers. Polymer brushes are grown via “grafting from” atom-transfer radical polymerization after activation of the PET surface with 3-aminopropyltriethoxysilane. Spectroscopic analyses confirm the expected reactions at each reaction step, as well as the ultimate growth of brushes on the PET microfibers. Post-polymerization modification reactions have likewise been conducted to further functionalize the brushes and impart surface properties of biomedical interest on the PET microfibers. Antibacterial activity and protein resistance of PET microfibers functionalized with PDMAEMA and PHEMA brushes, respectively, are demonstrated, thereby making these surface-modified PET microfibers suitable for filtration media, tissue scaffolds, delivery vehicles, and sensors requiring mechanically robust support media.

Introduction

Electrospinning produces solid polymer fibers with diameters ranging from several tens of nanometres up to several microns. These nano/microfibers possess a high ratio of surface area to volume and are typically organized in high-porosity mats that are suitable for use in a broad range of applications involving (but not limited to) filters, sensors, nanocomposites, tissue engineering scaffolds, drug delivery vehicles, and energy storage media.6,7 During electrospinning, a polymer solution or melt with acceptable viscosity and conductivity levels is subjected to an electric field acting between a syringe needle and a collector plate. When electrostatic forces overcome the surface tension of the liquid at the tip of the needle, a charged polymer solution/melt jet is emitted from the resulting conical structure known as the Taylor cone.8 The jet undergoes a whipping process during which any solvent present evaporates, and the polymer is commonly collected as a dry, randomly oriented fiber mat on the grounded collector plate.9 Electrospinning represents an appealing and facile means of nano/microfiber production due to its relatively straightforward setup and the ability to independently tune fiber properties on the basis of both solution/melt characteristics and process parameters.

Although the structural features of electrospun nano/microfibers are advantageous, the bulk properties of such fibers tend to lack the (multi)functionality that is needed for many technologies. One way to overcome this problem is to create composite nano/microfibers by incorporating chemically and/or physically different species (molecules or nanoparticles) into the fibers to enhance, for example, mechanical,9 electrical,10 magnetic,12 or optical13 properties. Because functional species intended for use on polymer surfaces often exhibit reduced surface activity when incorporated in a polymer matrix prior to electrospinning, they may not always locate at the surface where their functionality is desired.14 For instance, when antibacterial biocides are added to a polymer prior to electrospinning, their efficacy is greatly compromised, and they may become unable to attack airborne pathogens.15 Sun et al.16,17 have, however, established that polarizable peptide-containing copolymers added to a polymer prior to electrospinning can be brought to the surface of nano/microfibers by the applied electric field, thereby resulting in fibers that are concurrently electrospun and biofunctionalized. Alternatively, the surface of electrospun nano/microfibers can be modified through the covalent bonding of poly(quinuaternary ammonium), which likewise creates a permanent antibacterial surface.18

Because polymer surfaces typically possess low surface energy, they must be pretreated chemically or physically to obtain an
active surface suitable for subsequent functionalization. Physical methods by which to activate a polymer surface include plasma treatment, ‘layer’ formation, UV treatment, mineralization, etching, or inclusion of a reactive composite material. Once chemically-active groups reside on the surface, covalent bonding, immobilization, and electrostatic interactions can be used to attach reactive groups to the fiber surface. Agarwal et al. have recently provided an extensive overview of various chemical methods by which to functionalize the surface of electrospun nanofibers for diverse applications ranging from functional textiles, catalyst supports and ion-exchange membranes to drug delivery and tissue engineering.

Modification of the fiber surface can make commodity and engineering plastics in particular suitable for applications wherein the fibers interact with their environment, such as molecular filtration, protective textiles, tissue scaffolds, and drug delivery. A synthetic polymer that shows particular promise in this regard is poly(ethylene terephthalate) (PET), and electrospun PET microfibers have already been considered in applications that benefit from the mechanical strength and solvent resistance of PET. As with most organic polymers, however, PET does not possess good adhesion and wetting properties because of its inherently low surface energy (42 mJ m⁻²). Application of electrospun PET microfibers as functional materials therefore necessitates alteration of their surface properties without compromising bulk characteristics.

Modification of PET surfaces has been conducted by a variety of chemical methods, including chemical treatment (e.g., hydrolysis, reduction, aminolysis, glycosylation, polyelectrolyte deposition, surface graft polymerization after surface activation) and physical modification (e.g., plasma, ultraviolet/ozone, flame, corona treatment, electrical discharge, ion beam bombardment, and laser treatment). Since most of these surface modification techniques involve, purposefully or inadvertently, polymer degradation, careful selection of experimental conditions is imperative for the successful surface modification of ultrafine PET microfibers without degrading the bulk polymer and its desirable mechanical properties. Grafting polymer brushes on surfaces represents a generally attractive approach by which to modify and control the surface properties of materials. Surface-initiated graft polymerization has been performed successfully on flat surfaces with a variety of monomers and polymerization methods. Specifically, atom transfer radical polymerization (ATRP) has been employed extensively because (i) its controlled implementation does not require ultrapurification of the chemicals used, and (ii) it can be used to polymerize numerous functional monomers, such as N-isopropylacrylamide (NIPAAm), 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA), as well as others.

Graft polymerization on PET surfaces has been reported by Roux and Demoustier-Champagne and Bech et al. (for styrene), as well as Farhan and Huck (for NIPAAm). These efforts employ various means of attaching surface initiators for “grafting from” polymerization. For instance, Roux and Demoustier-Champagne have attached free-radical polymerization initiators to the surface of PET via electrostatic interactions and covalent bonding after surface activation by saponification and oxidation. Farhan and Huck and Bech et al. have alternatively attached ATRP initiators after activating the PET surface by plasma treatment and aminolysis, respectively. The major drawback of these approaches — viz., saponification, aminolysis, and plasma treatment — is that they often induce severe degradation of PET and promote a roughened surface topography. Because of the nano/micrometre dimensions of electrospun PET fibers, it is paramount that material degradation and surface roughening must be minimized.

The quantity of studies devoted to electrospun PET fibers is rather limited despite the abundance of reports on electrospinning other polymer solutions and melts. We have sought to craft a mild and universal means by which to modify the surface of electrospun PET fibers so as to combine the mechanical robustness of PET with the functionality of polymer brushes. In this work, we have elected to functionalize PET microfiber surfaces by means of 3-aminopropytriethoxysilane (APTES). Bui et al., Fadeev and McCarthy, and Xiang et al. have demonstrated that the primary amine group in APTES inserts into the PET chain via an amidation reaction with negligible degradation to bulk PET. In this reaction mechanism the triethoxysilane groups of APTES are exposed at the air interface, and subsequent hydrolysis of the ethoxysilane units yields silanol groups on the PET surface. These groups are suitable as attachment points for an ATRP initiator, such as [11-(2-bromo-2-methyl)propionoxy]undecyltri chlorosilane (BMPUS). We use this approach to grow poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) brushes on electrospun PET microfibers, along with a battery of analytical techniques to characterize the properties of electrospun PET microfibers before and after surface polymerization of DMAEMA and HEMA via ATRP. We also investigate the post-polymerization modification of the corresponding PDMAEMA and PHEMA brushes via quaternization and fluorination, respectively, and demonstrate the antibacterial and protein-resistance properties of these functionalized PET microfiber mats.

Experimental

Materials

Food-grade recycled PET flakes were kindly supplied by United Resource Recovery Corporation (Spartanburg, SC). Anhydrous toluene, 2-chlorophenol, methanol, iodomethane, iodopropene, iodobutane, bromoethane, bromopropane, bromobutane, trifluoroacetic anhydride (TFAA), fibrinogen from human plasma, 1X-PBS buffer (0.137 M NaCl, 0.0027 M KCl, and 0.0119 M phosphates), APTES, DMAEMA, HEMA, Cu(0) bromide (CuBr), Cu(I) bromide (CuBr₂), Cu(I) chloride (CuCl), Cu(I) chloride (CuCl₂), bipyridine, and N,N,N’,N’-pentamethyldiethylenetriamine (PMDETA) were all purchased from Sigma-Aldrich (St. Louis, MO) and used as-received. Hexafluoroisopropanol (HFIP) was obtained from Oakwood Products Inc. (Estill, SC).

Brush growth/modification

The PET flakes were dissolved in HFIP at different polymer concentrations and electrospun at 10 kV to generate microfibers
varying in diameter. Thin PET films measuring 12 and 180 nm thick were spin-coated on silicon wafers from 0.5 and 3 wt% solutions, respectively, in 2-chlorophenol. The latter specimens allowed us to follow each modification step by measuring film thickness increments associated with the various chemical modification steps and protein adsorption. Fiber mats and thin films were kept under vacuum for at least 48 h prior to use to remove entrapped solvent. Utilization of ATRP without sacrificial initiator allowed initiation of PDMAEMA and PHEMA from only the PET microfiber surface, thereby precluding the formation of free PDMAEMA and PHEMA chains in the polymerization solution. The initiator for ATRP was BMPUS, synthesized as described earlier and deposited on the surface of PET microfibers and films after activation of the surface with APTES. Polymer brushes composed of either PDMAEMA or PHEMA were subsequently grown from the BMPUS-decorated PET surfaces by ATRP according to established protocols. For instance, 10.09 g HEMA was mixed with 6.81 g of methanol, 1.88 g of water and 0.63 g of bipyridine in an Ar-purged Schlenk flask, and oxygen was removed via three freeze-thaw cycles. After removal of oxygen, CuCl (0.18 g) and CuCl2 (0.01 g) were added to the solution and 1 more freeze-thaw cycle was performed. This ATRP solution was transferred to a tightly sealed Schlenk flask, which was stored in an Ar-purged glove box. Fiber mats and films decorated with BMPUS were placed in a separate Schlenk flask, which was evacuated to remove oxygen and backfilled with Ar. The flask was transferred to an Ar-purged glove box where the initiator-deposited fiber mats and films were submerged in the ATRP solutions for 6 and 8 h to produce PDMAEMA and PHEMA brushes, respectively. After removal from the ATRP solution, the samples were rinsed promptly with methanol and deionized water, and then sonicated in deionized water for 10 min.

The PDMAEMA brushes grown on PET microfibers and silicon wafers were quaternized with iodomethane, iodopropane, iodobutane, bromoethane, bromopropane, and bromobutane in acetonitrile at 60 °C for ≈20 h. An excess amount of quaternization agents was added to the glass vial containing PDMAEMA-modified PET microfiber mats and acetonitrile to yield fully quaternized (q) PDMAEMA brushes. In similar fashion, the PHEMA brushes were fluorinated with TFAA to discern the effect of fluorinated (f) PHEMA on protein adsorption. In this case, TFAA was used to bind fluorinated moieties to the hydroxyl terminus of the HEMA pendant group. All reactions were conducted at ambient temperature in the gas phase, and the samples were washed with copious amounts of ethanol and water and dried under reduced pressure before protein adsorption experiments. In both of the post-polymerization modification reactions listed above, bare (i.e., brush-free) PET microfibers were immersed in the post-polymerization modification reaction mixtures as controls.

**Material characterization**

The thicknesses of the PET films deposited on silicon wafer were measured with variable-angle spectroscopic ellipsometry (VASE, J.A. Woollam) at an incidence angle of 70° (between the beam and the surface normal) before and after each modification step to measure the approximate PDMAEMA and PHEMA brush thicknesses on the PET microfibers. In addition, the thickness of the polymer brushes after quaternization, fluorination, and protein adsorption was also measured with VASE to determine the extent of these post-polymerization modification steps. The surface chemical composition of modified microfibers was measured after each modification step by X-ray photoelectron spectroscopy (XPS) performed on a Kratos Axis Ultra DLD spectrometer at a take-off angle of 90° (under these conditions the probing depth of XPS is estimated to be ≈9–10 nm). Fourier-transform infrared (FTIR) spectroscopy was utilized to monitor chemical changes that occurred on the surface of the PET microfibers after modification. Spectra were recorded on a Nicolet 6700 spectrometer after embedding microfiber mats in KBr pellets for analysis in transmission mode, and resulting data were analyzed by the Omnic Specta software. For each sample, 1024 scans were collected at a resolution of 4 cm⁻¹. As-spun and surface-modified PET microfibers were coated with ≈8 nm of Au, and their diameter and surface morphology were examined by field-emission scanning electron microscopy (SEM) performed on a JEOL 6400F electron microscope operated at 5 kV. The average fiber diameter and corresponding standard deviation were determined by measuring the diameters of 100 fibers with the ImageJ software package.

**Antibacterial activity**

The PET microfibers decorated with a qPDMAEMA brush were subjected to antibacterial testing using a modified ASTM standard (E2149-01 Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents under Dynamic Contact Conditions). Here, *E. coli*, a model gram-negative bacterium, was grown in a Luria-Bertani (LB) medium overnight to yield a bacteria population of 5 × 10⁸ according to UV-Vis spectrophotometry. After serial dilutions, the modified PET microfiber mats (measuring ≈1 cm² in area) were incubated in a suspension containing 3 × 10⁸ bacteria in sterile conical tubes at 37 °C while being shaken at 300 rpm for 1 h. The resultant suspension was then diluted with LB medium to a desired concentration and spread on L-agar plates. The L-agar plates were incubated at 37 °C for 18 h. Each surviving cell developed into a distinct bacterial colony and provided information regarding bacterial activity. The number of viable cells was measured in terms of colony forming units (CFUs) on each plate.

**Protein resistance**

A 0.1 mg ml⁻¹ solution was prepared at the isoelectric point of fibrinogen (FIB, at pH = 5.5) by dissolving FIB in 1X-PBS buffer solution (0.2% NaN₃ was added to the buffer to prevent bacterial growth). The solution was passed through a 0.2 μm filter, and adsorption studies of FIB were conducted by incubating substrates in protein solution for 16 h at ambient temperature. Both fluorinated and unmodified PHEMA brushes on PET microfibers and films were tested alongside bare PET microfibers and films. After incubation, samples were washed thoroughly with deionized water, dried under reduced pressure and stored in glass vials for further characterization. The thickness of the adsorbed FIB layer was measured by VASE on flat samples (PET
films on silicon wafers), and the corresponding nitrogen surface concentration was measured by XPS to ascertain the amount of adsorbed FIB.

Results and discussion

The diameters of electrospun PET microfibers, prepared according to the protocol provided in the Experimental section and measured by SEM, are 450 ± 100, 800 ± 200 and 1200 ± 300 nm for 6, 8 and 10 wt% solutions, respectively, of PET in HFIP. While these standard deviations are relatively low, fiber diameters range from 300 nm to 3 μm. The surfaces of unmodified PET microfibers appear consistently smooth, as is evident in Fig. 1. Functional PDMAEMA and PHEMA brushes have been grown on PET microfibers in the sequence of four steps reported earlier32 for PNIPAAm brushes. Briefly, APTES molecules are attached to the PET surface via aminolysis between PET and the primary amine of APTES. Next, the ethoxysilane groups on APTES are hydrolyzed to generate silanol groups for BMPUS attachment. Finally, PDMAEMA and PHEMA brushes are grown directly from the PET microfiber surface via ATRP.

As reported previously by Bui et al.37 and Fadeev and McCarthy,70 the primary amine group in APTES reacts with the ester functionality in PET by forming an amide bond via aminolysis (cf. Fig. 1). Both studies claim that aminolysis of PET with APTES does not degrade bulk PET as opposed to aminolysis of PET with short alkyl amines, since the latter can diffuse into a PET fiber and react all the way through, and thus weaken, the fiber.34,38 The presence of bulky triethoxysilane group on APTES molecules hinders the diffusion of APTES into PET by increasing the size of the molecule, changing the solubility of the alkyl amine to which it is attached and creating a protective surface layer (which serves to impede the diffusion of other APTES molecules). While neither Fadeev and McCarthy70 nor Howarter and Youngblood71 could detect the formation of amide groups on PET due to the small population of amide groups available on their flat samples, the presence of amide groups on PET-SiOH microfiber surfaces has been directly confirmed via FTIR analysis by Özçam et al.32 as a result of the enlarged surface area afforded by electrospun PET microfibers. The appearance of new peaks at 1650 (amide I band), 1550 (amide II band), 3300, 1470, and 3300 cm⁻¹ are attributed to the formation of secondary amide groups on the surface of PET microfibers. The formation of silanol groups upon hydrolysis of the ethoxysilane groups also contributes to the band located at 3300 cm⁻¹.74 Attachment of APTES, followed by hydrolysis of the exposed triethoxysilane groups in acidic water (pH ≈ 4.5–5.0), yields further reactive silanol groups, as indicated by both a decrease in water contact angle (WCA) and associated thickness measurements performed on flat PET films on silicon wafers. For instance, the WCAs of APTES-modified PET and virgin PET films are 50° ± 0.8° and 71° ± 0.8°, respectively, after exposure to acidic water, in contrast to the WCA of native PET (75° ± 0.2°). In addition, XPS spectra collected from PET-SiOH microfibers confirm the existence of a small nitrogen N₁s, Si₂s and Si₂p peaks at 399.7, 153.1 and 101.8 eV, respectively, which correspond to 0.6 atom% nitrogen and 1.1 atom% silicon present on the PET-SiOH surface.

Attachment of BMPUS molecules to the PET-SiOH surface as initiator centers for “grafting from” polymerization of
DMAEMA and HEMA, followed by the ATRP conditions described in the Experimental section, results in the formation of dry brushes measuring \( \approx 50 \) and \( \approx 45 \) nm thick, respectively, as determined by VASE analysis of thin spin-coated PET films on silicon wafers. Here, we assume that the thicknesses of brushes grown on silicon wafers is comparable to that produced on the microfibers, since the microfibers are relatively large and possess negligible curvature on the size scale of the brushes. Examples of PET microfibers after brush growth are presented in Fig. 2 and verify that the chemical reactions undertaken have no discernible effect on microfiber morphology. Corresponding FTIR spectra of the polymer brushes, along with spectra acquired from electrospun PET and PDMAEMA and PHEMA brushes grown directly on silicon wafers, are provided in Fig. 3. The spectra of PDMAEMA and PHEMA brushes on silicon wafer are included to point out the chemical changes that occur on the PET microfibers. Careful comparison of these spectra confirms that PDMAEMA and PHEMA brushes grew from the surface of PET microfibers. The appearance of new stretching vibrations located at 2770 and 2820 cm\(^{-1}\) for the PDMAEMA brush (blue line in Fig. 3a), for instance, reflects the C–H bond of the \(-\text{Ni}(\text{CH}_3)_2\) group of PDMAEMA. Likewise, the increase in peak intensity at \( \approx 3400 \) cm\(^{-1}\) for the PHEMA brush (blue line in Fig. 3b) is a consequence of the broad –OH peak originating from PHEMA.

The chemical compositions of PDMAEMA and PHEMA brushes grown from the surface of PET microfibers have been assessed by XPS, and resulting values are listed in Table 1. The theoretical values of these compositions are calculated on the basis of the number of atoms present on each repeat unit of both polymers and the assumption that the brush thickness is larger than the probing depth of XPS (\( \approx 10 \) nm). Representative XPS spectra of PET microfibers with grafted PDMAEMA and PHEMA brushes are plotted for comparison in Fig. 4. Bare PET exhibits 2 ionization peaks, one for carbon (at 285 eV) and the other for oxygen (at 536 eV). Corresponding surface concentrations, computed from the areas under these curves, are 73.2 ± 0.4 (71.4) and 26.8 ± 0.4 (28.6) atom% for carbon and oxygen, respectively, which agree favorably with the theoretical values provided in parentheses. On one hand, growth of a PDMAEMA brush on the surface of PET microfibers is responsible for the appearance of the nitrogen peak at 399.7 eV (cf. Fig. 4b). Quantitation of such XPS spectra results in surface concentrations of 73.6 ± 0.5, 7.6 ± 0.1 and 18.8 ± 0.5 atom% for carbon, nitrogen and oxygen, respectively. Introduction of a PHEMA brush, on the other hand, does not change the number or the position of the peaks recorded in XPS spectra. Instead, the relative peak areas are affected so that the surface concentrations become 70.3 ± 0.5 and 29.7 ± 0.5 atom% for carbon and oxygen, respectively. These concentration values measured experimentally for PDMAEMA and PHEMA brushes grown on PET microfibers are in good quantitative agreement with the theoretical values determined on the basis of the chemical structures of the individual species (cf. Table 1).

Ellipsometry measurements of flat PET films on silicon wafer, in conjunction with independent XPS measurements conducted on PET microfiber surfaces, suggest that the polymer brushes completely cover the PET surfaces, since the dry thicknesses of the brushes exceed the probing depth of XPS. The characteristic XPS “fingerprint” of PET disappears from the high-resolution spectra (displayed in the insets of Fig. 4) after growing the PDMAEMA and PHEMA brushes. Introduction of the peak corresponding to the C–N bond at 286.1 eV serves to broaden the peaks at 285.0 (the C–C bond) and 286.6 eV (the C–O bond) for the PDMAEMA brush grown on PET microfibers. In the case of the PHEMA brush, the intensity of the peak located at 286.6 eV is larger than that at 285.0 eV relative to the XPS spectrum of bare PET. The peak at 290.0 eV, which corresponds to the O–C==O groups of acrylates, is present for both PDMAEMA and PHEMA brushes grown on the PET microfibers.35

Post-polymerization modification reactions have been performed on the PDMAEMA and PHEMA brushes grafted to the surface of PET microfibers to introduce antibacterial and protein resistance properties, respectively. One of the potential applications of PDMAEMA after quaternionization of the dimethylamino groups on the DMAEMA repeat unit is as an antibacterial...
material. Polymer chains quaternized with alkyl halides possess positive charges and hydrophobic alkyl chains, which induce cation exchange and penetration through the bacterial cell membrane, respectively. These result in disruption of membrane integrity and death of bacterial cells. Antibacterial properties of quaternary ammonium compounds (QACs) have been reported earlier in solution and on solid surfaces. The latter has an important advantage over free QACs because they are covalently attached to substrates, which, in turn, permit repeated use with limited biocidal release to the environment. Quaternization of the PDMAEMA brush grown on the surface of PET microfibers has been achieved with alkyl bromides differing in length to yield a polycationic brush. Conversely, the PHEMA brush can be modified to resist protein adsorption, which remains a significant challenge in biomedical applications involving artificial implants. Adsorption of biomass on the surface of functional materials degrades surface functionality over time. Biomass accumulation begins with protein adsorption and denaturation on any surface with which proteins come in contact. Protein adsorption on various surfaces has been studied extensively over the past several decades, and the incorporation of ethylene glycol and fluorinated units into polymeric coatings have been found to be among the most effective at reducing the propensity for protein adsorption.

In the present study, several quaternization agents differing in alkyl length—iodomethane, iodopropane, iodobutane, bromoethane, bromopropane, and bromobutane—have been used to introduce positive charges into the PDMAEMA brush grown on PET microfibers and generate a polycationic qPDMAEMA brush with antibacterial properties. Similarly, TFAA has been used to fluorinate the –OH groups of the PHEMA brush so that the effect of fPHEMA on the protein resistance of functionalized PET microfiber mats can be probed. The morphologies of PET microfibers after these post-polymerization modification reactions are visible in Fig. 5 and verify that a microfibrinous network of the electrospun mat is retained. Chemical modification of PDMAEMA and PHEMA brushes grown on silicon wafers (not on PET film) with quaternization and fluorination agents, respectively, results in multiple changes in the FTIR spectra. For example, the stretching vibrations located at 2770 and 2820 cm$^{-1}$ for the PDMAEMA brush in Fig. 6a are attributed to the C–H bond of the –N(CH$_3$)$_2$ group. These peaks disappear completely after quaternization. Water absorbed by the more hydrophilic qPDMAEMA brush is responsible for the appearance of the peak located at $\approx$ 3400 cm$^{-1}$. New peaks reflecting the formation of C–CO–CF bonds (at 1789 cm$^{-1}$) and C–F bonds (at 1224 and 1157 cm$^{-1}$) likewise appear after conversion of PHEMA to fPHEMA in Fig. 6b. Moreover, the –OH groups of PHEMA are consumed during the fluorination reaction with TFAA, and the peak located at $\approx$ 3400 cm$^{-1}$ disappears. It is noteworthy that the FTIR spectra collected from PDMAEMA and PHEMA brushes grown on silicon wafers before and after quaternization (PDMAEMA) and fluorination (PHEMA) possess the same characteristic peaks in Fig. 6, thereby providing evidence that the brushes grown on the PET microfibers are functionalized.

### Table 1

Compositions of PET microfiber surfaces with grafted PDMAEMA and PHEMA brushes from XPS analysis

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Concentration (atom%)</th>
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<tr>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>PET microfiber</td>
<td>Theoretical</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>PDMAEMA brush</td>
<td>Theoretical</td>
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<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>PHEMA brush</td>
<td>Theoretical</td>
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<td>Experimental</td>
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Fig. 4 XPS spectra collected from (a) electrospun PET microfibers, as well as PET microfibers functionalized with (b) PDMAEMA and (c) PHEMA brushes. A high-resolution carbon-edge spectrum is included in the inset of each panel.

Fig. 5 SEM images acquired from electrospun PET microfibers with post-functionalized (a) qPDMAEMA (using bromobutane) and (b) fPHEMA brushes. The solution concentration used to generate the PET microfibers displayed here was 8 wt% PET in HFIP.
The chemical compositions of brushes grown on PET microfibers and silicon wafers after quaternization and fluorination reactions have been measured by XPS. Examination of the corresponding XPS spectra (data not shown) reveals the appearance of new peaks for iodine or bromine after quaternization of PDMAEMA and fluorine after fluorination of PHEMA. Quantitation of these spectra yields the surface concentrations listed in Table 2 for qPDMAEMA (with alkyl bromides) and Table 3 for fPHEMA. Interestingly, the concentration of bromine in the qPDMAEMA brush grown on PET microfibers is up to \( z \geq 50\% \) greater than that in the qPDMAEMA brush on silicon wafer. While this difference was initially attributed to the adsorption or absorption of alkyl bromides on/in PET, XPS spectra obtained from bare PET microfibers exposed to the quaternization medium for the same reaction time reveal no existence of bromine. Therefore, we propose that this difference is a result of the curved nature of the PET microfibers, which apparently possess a lower steric hindrance (due to the higher surface area) for the quaternization reaction as compared to a flat surface. The same trend is also observed for the quaternization reaction of PDMAEMA brushes with alkyl iodides. In contrast, the extent of fluorination of the PHEMA brush grown on PET microfibers and silicon wafers is similar, and these values are in agreement with those reported earlier for TFAA-modified PHEMA brushes. This observation, which differs from the results obtained for qPDMAEMA brushes, may be due to the smaller size of TFAA relative to the alkyl halides and the gas-phase reaction of TFAA (wherein TFAA molecules can diffuse through the brush and completely react with all available –OH groups without restriction). Arifuzzaman et al. have demonstrated that the surface concentration of TFAA-modified PHEMA brushes on silicon wafer does not change as a function of XPS take-off angle, which evinces that (i) PHEMA brushes react homogeneously throughout the XPS probing depth and (ii) the gas-phase reaction of TFAA is quantitative with PHEMA brushes irrespective of the substrate on which they are grown. We hasten to add that exposure of bare PET microfibers to TFAA did not alter the surface composition of the bare PET, according to XPS analysis.

The presence of QACs endows the surface of the PET microfibers with antibacterial properties due to the presence of cationic groups that disrupt cell membranes and induce bacterial lysis. In the case of gram negative bacteria such as *E. coli*, the phosphate groups of lipopolysaccharide molecules located in the outer bacterial membrane are stabilized by divalent cations, which would otherwise strongly repel each other, via bridging and neutralizing. Bacteria lose their natural counterions and their outer membrane is destabilized upon interacting with QACs due to the electrostatic compensation of these charges with the cationic charges of the QACs. Thus, the release of counterions from the outer cell wall initiates the death of the bacteria. Quaternization of the PDMAEMA brush on PET microfibers with alkyl bromides differing in methylene length produces string (quenched) polycationic brushes on the microfiber surface. As reported earlier, the antibacterial efficacy of a QAC depends on the extent of quaternization, as well as the length of the alkyl chain in the quaternization agent. The extent of quaternization dictates the number of positive charges available to interact with the bacterial membrane, whereas the length of the alkyl chain mediates the packing of the brush on the microfiber surface and affects the accessibility of the QACs to the bacterial cell membrane.

### Table 2  Compositions of PET microfiber surfaces and silicon wafer modified with grafted PDMAEMA brushes after quaternization

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Concentration (atom%)</th>
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<tr>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>qPDMAEMA on PET microfiber with bromoethane</td>
<td>73.9</td>
</tr>
<tr>
<td>qPDMAEMA on silicon wafer with bromoethane</td>
<td>71.2</td>
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<tr>
<td>Bromoethane on PET microfiber (control)</td>
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<tr>
<td>qPDMAEMA on PET microfiber with bromopropane</td>
<td>74.6</td>
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<tr>
<td>qPDMAEMA on silicon wafer with bromopropane</td>
<td>72.4</td>
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<tr>
<td>Bromopropane on PET microfiber (control)</td>
<td>73.7</td>
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<tr>
<td>qPDMAEMA on PET microfiber with bromobutane</td>
<td>74.0</td>
</tr>
<tr>
<td>qPDMAEMA on silicon wafer with bromobutane</td>
<td>73.5</td>
</tr>
<tr>
<td>Bromobutane on PET microfiber (control)</td>
<td>72.6</td>
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</table>
alkyl chain affects the antibacterial efficacy by governing the depth of penetration through the cell wall. In general, antibacterial efficiency increases as the length of the alkyl spacer is increased, but deteriorates after 6 methylene units. As seen in Fig. 7a, the presence of a polycationic qPDMAEMA brush on PET microfibers provides antibacterial properties against *E. coli* as the number of CFUs on the agar plates with qPDMAEMA-modified microfibers is lower than on those with PDMAEMA-modified microfibers. In addition, the antibacterial efficiency of the qPDMAEMA brush increases substantially with increasing alkyl length of the quaternization agent from bromoethane to bromobutane, as indicated by the results provided in Fig. 7b.

The resistance of PHEMA and iPHEMA brushes to protein adsorption on flat surfaces has been recently investigated, and the presence of PHEMA® and iPHEMA® brushes has been found to reduce protein adsorption, depending on the graft density and molecular weight of the brush. In this work, we only examine the protein resistance of a PHEMA brush grown on PET microfibers before and after fluorination with TFAA. Several different samples including PHEMA brushes on PET microfibers, iPHEMA brushes on PET microfibers, PHEMA brushes on silicon wafer, iPHEMA brushes on silicon wafer, bare PET microfibers and bare PET microfibers exposed to TFAA have all been incubated in FIB solution for 16 h. Adsorption of FIB on flat substrates has been monitored by measuring the brush thickness with VASE (on silicon wafers) and the surface nitrogen concentration (due to FIB) with XPS (on fibers and silicon wafers). Comparing the FIB layer thickness on flat surfaces reveals that the presence of a PHEMA brush dramatically reduces protein adsorption. According to the results presented in Fig. 8, the thickness of FIB plummets from ≈4 nm to almost 0 nm in the presence of a PHEMA brush, and this reduction is corroborated by XPS data that confirm a corresponding decrease in nitrogen concentration from 15.1 to 0.6 atom%. The amount of FIB adsorbed on spin-coated PET microfibers is lower than that on untreated microfibers.

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPHEMA on PET microfiber</td>
<td>54.4</td>
<td>25.0</td>
<td>20.6</td>
</tr>
<tr>
<td>iPHEMA on silicon wafer</td>
<td>53.2</td>
<td>24.6</td>
<td>22.2</td>
</tr>
<tr>
<td>TFAA-treated PET microfiber</td>
<td>74.2</td>
<td>25.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Fig. 7** In (a), photographs of *E. coli* colonies on L-agar plates containing bare PET microfibers, as well as PET microfibers modified with a PDMAEMA brush and post-quaternized with bromoethane, bromopropane and bromobutane (labeled) after an incubation period of 18 h at 37 °C. The dependence of the number of colony forming units (CFUs) on the length of the alkyl bromide used is evident in (b). For reference, the CFU corresponding to the bare PET microfibers is indicated by the red line.

**Fig. 8** Surface nitrogen concentration (left ordinate, red bars) and fibrinogen thickness (right ordinate, blue squares) for various systems containing silicon wafer, electrospun PET microfibers, PHEMA brushes and post-functionalized iPHEMA brushes.
film is comparable to that adsorbed on bare silica wafer, but the concentration of adsorbed FIB on bare PET microfiber (with and without TFAA treatment) is noticeably lower than that on spin-coated PET film. Introduction of a PHEMA brush on PET microfibers effectively prevents FIB adsorption, but fluorination of the brush does not appear to afford further improvement. In contrast, fluorination of the PHEMA brush grown on silicon wafer slightly improves protein resistance, as discerned from both thickness and XPS results.

Conclusions

In this work, we have demonstrated that the surface of electrospun PET microfibers can be controllably modified via the amidation reaction of the amine group on APTES with the ester group of PET and subsequent growth of functional polymer brushes (PDMAEMA and PHEMA) by ATRP. Post-polymerization modification of these brushes has been conducted by quaternization (PDMAEMA) and fluorination (PHEMA) reactions. None of these brush-growing or post-functionalization reactions have any discernible deleterious effect on the morphology of the PET microfibers and, by inference, their robust mechanical properties. The improved antibacterial efficacy of quaternized PDMAEMA brushes and protein resistance of (fluorinated) PHEMA brushes grown on PET microfibers are established. These functional microfiber mats are suitable for use as affinity filters, antibacterial clothing and responsive sensors. Specifically, we envisage that these modified PET microfiber mats can be employed as multi-use filters for water purification applications, in which case the stability of such brushes must be ascertained as a function of pH and temperature. In this and related technologies, the ability of surface-modified microfibers to withstand environmental stresses is of paramount importance, which is why we have elected to use electrospun PET microfibers and why we have chosen a chemical reaction route that does not compromise the mechanical robustness of PET.

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