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Electrospinning of polymer nanofibers with specific surface chemistry

J.M. Deitzel[a], W. Kosik[a], S.H. McKnight[a], N.C. Beck Tan[a,*], J.M. DeSimone[b], S. Crette[b]

[a]*US Army Research Laboratory, Polymers Research Branch, AMSRL-WM-MA, APG, MD 21005, USA*

[b]*Department of Chemistry University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA*

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Abstract

Electrospinning is a process by which sub-micron polymer fibers can be produced using an electrostatically driven jet of polymer solution (or polymer melt). Electrospun textiles are of interest in a wide variety of applications including semi-permeable membranes, filters, composite applications, and as scaffolding for tissue engineering. The goal of the research presented here is to demonstrate that it is possible to produce sub-micron fibers with a specific surface chemistry through electrospinning. This has been accomplished by electrospinning a series of random copolymers of PMMA-*r*-TAN from a mixed solvent of toluene and dimethyl formamide. X-ray Photoelectron Spectroscopy (XPS) analysis shows that the atomic percentage of fluorine in the near surface region of the electrospun fibers is about double the atomic percentage of fluorine found in a bulk sample of the random copolymer, as determined by elemental analysis. These results are in good agreement with XPS and water contact angle results obtained from thin films of the same copolymer materials. © 2001 Published by Elsevier Science Ltd.

Keywords: Electrospinning; Random copolymer; Surface segregation

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1. Introduction

For the past few years, there has been growing interest in a novel fiber production technology known as electrospinning. Electrospinning is unique as a fiber spinning process because it can consistently generate polymer fibers ranging from 50 to 500 nm in diameter [1]. The fibers are formed using an electrostatically driven jet of polymer solution (or polymer melt), emitted from the apex of a cone formed on the surface of a droplet of polymer or polymer solution. As this jet travels through the air, it solidifies leaving behind a polymer fiber to be collected on an electrically grounded target. Because of the small fiber diameters, electrospun textiles inherently possess a very high specific surface area and small pore size. These properties make electrospun fabrics interesting candidates for a number of applications including membranes [2], tissue scaffolding and other biomedical applications [3], reinforcement in transparent composites [4], and nanoelectronics [5]. Most of the recent work [1–8] on electrospinning has focused either on trying to understand the fundamental aspects of the process in order to gain control of fiber morphology and structure or on determining appropriate conditions for electrospinning of various polymers. Given that most proposed applications exploit the high surface area of the fibers and textiles, methods for tailoring the chemistry of the electrospun fiber surface should be important to the eventual exploitation of the technology. Though efforts to control the surface chemistry of polymer thin films have been the focus of a great deal of research in the last decade [9–13], no studies of surface chemistry control in electrospun fibers have been documented.

Among the studies of surface chemistry control in polymer films, those focusing on the formation of fluorinated surfaces have been the most prevalent. Fluorinated surfaces are inherently of interest for stain resistant and water repellent materials and coatings applications. In addition, the surface activity of fluorinated groups may be used to draw adjacent groups of specific chemistry or functionality to a surface [14,15], which may prove critical for medical applications. Because fluorinated polymers are often difficult to process, design of non-wetting surfaces using fluorinated block copolymers or homopolymers that are terminated with a fluorinated end-cap is often employed [16]. Fluorinated chemical moieties in polymer and diblock copolymer materials have a natural tendency to segregate at the polymer's surface, minimizing the surface free energy of the film at the polymer/air interface [9–16]. Typically, scientific investigations of these materials have been conducted on thin films (~100–200 nm thickness), which are often annealed to encourage complete surface segregation.

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[*] Corresponding author. Current address: W.L. Gore & Associates, 501 Vieve's Way, Elkton, MD 21922, USA.

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Table 1
Molecular weight of PMMA homopolymer and PMMA-*r*-TAN copolymers, as determined by GPC

	PMMA	PMMA-*r*-TAN		
		99:1	95:5	90:10
M_w, g/mol	159,000	165,000	157,000	155,000
Polydispersity	2.1	1.95	2.1	2.2
Atomic% fluorine[a]	0.2	1.4	8.6	15.6

[a] As determined by elemental analysis.

The goal of the current research is to apply the lessons learned from research on fluorinated surface control in thin films to the processing of electrospun nanofibers demonstrating the tailoring of their surface chemistry.

2. Experimental details

A series of random copolymers of polymethylmethacrylate (PMMA) with varying tetrahydroperfluorooctyl acrylate (TAN) concentration (0–10% TAN) were synthesized by radical copolymerization in toluene using 0.1 wt% AIBN initiator, carried out over a period of 24 h at 70°C. Copolymer compositions were determined using elemental analysis (Galbraith Laboratories, Knoxville, TN) yielding fluorine concentrations indicative of a synthesis taken to 85% completion. Though reactivity ratios are not available for the methyl methacrylate–tetrahydroperfluorooctyl acrylate (MMA–TAN) system, consideration of reactivity for similar monomers suggest that this monomer pair would produce a copolymer in which an alternating structure would be favored over a blocky structure [17]. The molecular weights for the polymers, as determined by GPC, are given in Table 1.

Thin films were prepared by spin casting from 5 wt% solution in toluene onto clean silicon substrates followed by drying for 18 h at ambient temperature under vacuum. Film thickness ranged from 170 to 225 nm, as determined by X-ray reflectometry. Annealed films were treated under vacuum at 170°C for 8 h. Advancing and receding water contact angles were measured using an AST Inc. VCA 2000 Video Contact Angle System.

Fibers were electrospun from solutions of 10 wt% polymer in a solvent mixture containing 10% dimethyl formamide (DMF) and 90% toluene, by volume. Polymer solution was fed at approximately 1 ml/h through a stainless steel syringe pipette needle (18 gauge) carrying a potential bias of +5 kV. Fibers were collected on an electrically grounded aluminum target placed 4 in. below the syringe tip. The resulting fiber mats were then annealed at 120°C for 4 h under vacuum.

Micrographs of the electrospun materials were obtained with a Phillips-Electroscan Environmental Scanning Electron Microscope. Samples were mounted on copper tape attached to a standard stub and imaged at a working distance of 9 mm in a water vapor atmosphere at ambient temperature and chamber pressure of 4.3 Torr. The accelerating voltage of the electron beam was set at 12 kV.

Chemical analysis of the near surface region for both thin film and electrospun fiber samples was performed using a Kratos Axis 165 X-ray photoelectron spectroscopy system, equipped with a hemispherical analyzer. A 100 W monochromatic Al Kα (1486.7 eV) beam-irradiated 1 mm × 1/2 mm spot was used. All spectra were taken at a 2×10^{-9} Torr vacuum environment. Survey and elemental high resolution scans for C_{1s}, F_{1s} and O_{1s} were taken at pass energy of 80 eV for 5 min and pass energy of 40 eV for 2–8 min depending on the signal to noise ratio, respectively. To compensate for sample charging, a hybrid electrostatic and magnetic lens column with an integral coaxial charge neutralizer was employed to maintain uniform surface charge for the exact spot under examination. TAN has a photoemission cross-section 4 times that of C [18], resulting in increased charging observed with the increased TAN incorporation. Saturated hydrocarbon C_{1s} in the spectra were shifted by a correction factor ($\pm\delta$) to C1s BE = 285.0 eV. During the peak fitting routine, a 90/10 Gaussian–Lorentzian ratio was used and the full width at half maximum values were permitted to vary within theoretical and previously published regimes for similar polymer structures [20].

3. Results and discussion

Surface segregation was studied using a series of novel random copolymers of MMA and TAN with nominal TAN content varying from 0–10 mol%. Random copolymers have an advantage over block or end-capped fluorinated copolymers due to the simple synthesis and correspondingly low cost. Though some earlier work [11–13] has focused on the surface segregation of fluorine in thin films of low molecular weight random copolymers (6000 MW), to the best of our knowledge, this work is the first to demonstrate that high molecular weight random copolymers show significant enrichment of fluorine at a polymer surface. We studied the segregation phenomena first in thin films spin-cast on silicon substrates (as a control) and then in electrospun nanofiber textiles.

Surface properties of the thin films were analyzed using water contact angle measurements and X-ray photoelectron spectroscopy (XPS). Advancing contact angles increased from 76° for pure PMMA to 103° for the 90:10 P(MMA-*r*-TAN) copolymer for the as-cast films, and were slightly higher after annealing (Table 2). The measured ranges for both advancing and receding contact angles are similar to those reported for acrylic polymers modified with similar quantities of perfluorinated acrylic monomers that were found to have a large excess of the fluorinated component at the surface [12]. The highest contact angle measured in

Table 2
Water contact angles for thin films

	PMMA	PMMA-*r*-TAN		
		99:1	95:5	90:10
Unannealed				
Advancing	76	80	92	103
Receding	67	68	68	73
Hysterisis	9	12	24	30
Annealed				
Advancing	76	87	98	107
Receding	68	71	80	82
Hysterisis	10	16	18	25

this study, 107° for the annealed 90:10 P(MMA–TAN) film, approaches that typically measured for pure polytetrafluoroethylene surfaces (108–112°) [19]. The results are consistent with a high degree of fluorine segregation at the film surface resulting from the incorporation of a relatively small amount of fluorinated monomer randomly into the polymer.

A significant difference between the advancing and receding contact angles for the thin films was also observed. This contact angle hysteresis may reflect the presence of chemical heterogeneity at the film surface. It is very likely that the fluorinated moieties exist in small domains that are interspersed with large hydrocarbon moieties [11,12]. Other factors, such as surface roughness and the tendency of the fluorinated side chains to try to bury themselves in the presence of water [15], might also contribute to the contact angle hysteresis.

XPS analysis was performed on each of the films in order to quantify the amount of fluorine present in the near-surface region. Typical high-resolution C_{1s} spectra from fluorinated 90:10 P(MMA/TAN) and the (PMMA) control are shown in Fig. 1. The four functional species which contribute to the total C_{1s} peak in poly(methyl methacrylate), C–C (285 eV), C–C b-shifted (286.2 eV), C–O (286.8 eV) and O=C–O (289.4 eV), are identified. In the TAN polymers, two more peaks resulting from the CF_2 and CF_3 bonds are also evident. The spectral peaks corresponding to the oxygen moieties were also detected (not shown) in all polymers, and the copolymers had a single peak corresponding to the fluorine moiety. Only expected elements were detected. After appropriate linear background subtraction, the total C, O and F were quantified through an integration subroutine using the manufacturer's peak-fitting software. The individual peak fits agreed well with the expected structure and stoichiometry of the MMA–TAN systems.

Since the area under the peak is proportional to the number of atoms that contribute to a given intensity, it is possible to obtain the atomic% concentration of a given chemical moiety in the near surface region (~3 nm depth) of a film or fiber from the XPS data. This data is presented in Fig. 2, where the solid line, A, represents the atomic% F in the bulk polymers as determined by elemental analysis, and the dashed line, B, represents the near-surface atomic% F, as determined by XPS. The fluorine content in the near surface region of the thin films is approximately double that found for the bulk material, and reaches a maximum of ~25% in the 90:10 PMMA–TAN copolymer. For comparison, the surface concentration of pure poly(TAN) is ~58% F when

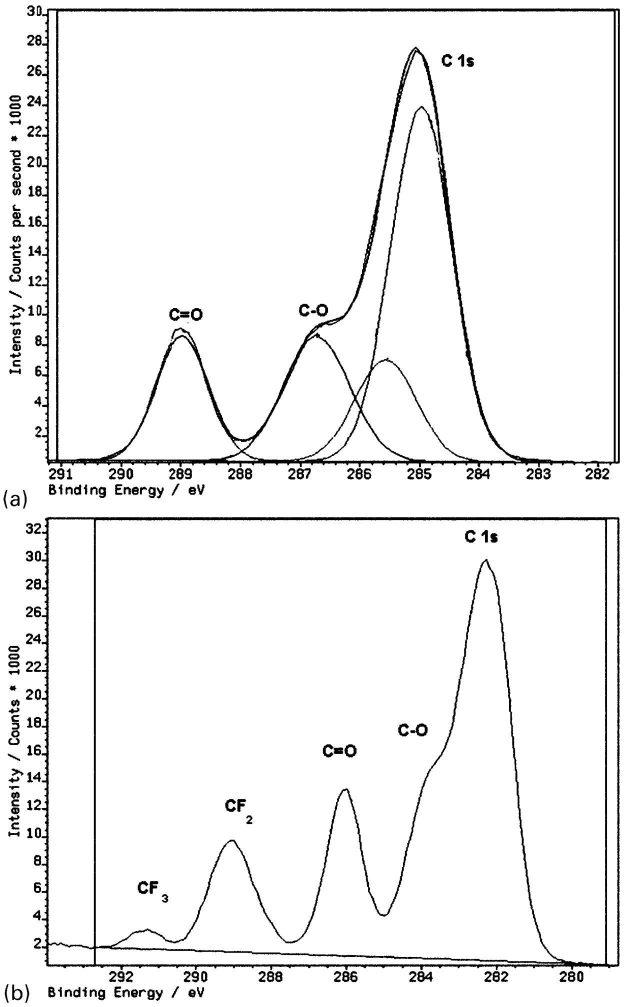

Fig. 1. XPS of the carbon region obtained from electrospun fiber mats; (a) PMMA homopolymer,(b) 90/10 PMMA-*r*-TAN copolymer.

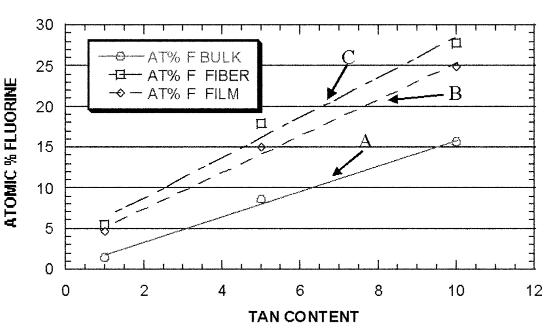

Fig. 2. Atomic percent content of fluorine as a function of TAN content; (a) bulk polymer (elemental analysis), (b) near surface for thin film (XPS), (c) near surface for electrospun fibers (XPS).

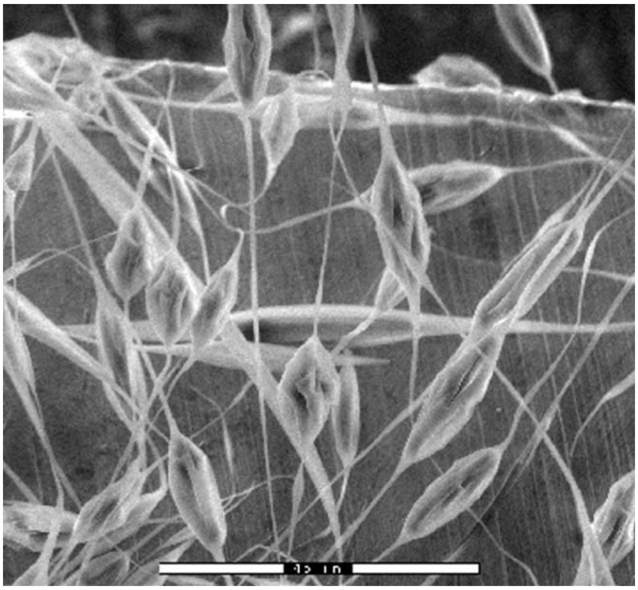

Fig. 3. Scanning electron micrograph of electrospun PMMA-*r*-TAN fibers.

measured under similar conditions [10]. While the observed doubling of the surface fluorine content is significant, it is less so in comparison to results of 3-fold to more than 60-fold increases reported by groups studying polymers with fluorinated end-groups [14,21] or copolymers with low molecular weight [11,12,20,21]. This is most likely due to the high molecular weight of the PMMA–TAN copolymers and the random placement of fluorinated groups, both of which have been shown to reduce the extent of segregation of surface active monomers [11,12,20–22]. It should be noted that earlier investigations of PMMA–TAN copolymers using angle-resolved XPS have shown that the fluorine content may reach as high as 42 atom% when measured at very low take-off angle, which would represent nearly a 3-fold excess [21].

Having proved the feasibility of obtaining a hydrophobic surface using a high molecular weight random copolymer, fibers of each of the random copolymers and the homopolymer control were electrospun and analyzed. The fiber diameters range from 0.3 to 2 μm (Fig. 3) for all samples examined, which is typical of electrospun fibers [1]. An interesting feature found in all the fibers was bead formation along their length. The beads observed have a wrinkled, 'raisin'-like surface texture that is different from the smooth ellipsoids that have been reported in the past [1,3,8,13]. This is most likely attributable to collapse of the ellipsoids after evaporation of the residual solvent. The bead morphology has been previously documented for electrospun fibers [1,3,8,13], and is affected by processing conditions [1,13]. A systematic study of processing parameters could readily identify conditions in which this characteristic would be eliminated.

The surface chemistry of the electrospun fibers was analyzed using XPS. The results, represented by line C in Fig. 2, demonstrate that significant surface segregation of the fluorinated species occurs in the electrospun fibers. The extent of segregation is similar to that observed in the thin films, e.g. the atomic% of fluorine in the near surface region of the electrospun fibers is roughly double the atomic percentage of fluorine in the bulk polymer. Additionally, it can be seen that the fluorine content measured for the fiber mats is always marginally higher than that of the thin films. This difference may be attributed to the distribution in take-off angles that occurs with non-planar specimens (e.g. a cylindrical fiber) in XPS, and is therefore most likely a measurement artifact rather than a genuine effect.

To summarize, it has been demonstrated that significant segregation of fluorine occurs at the surface of thin films of high molecular weight, fluorinated, random copolymers. At the highest TAN content measured, 10 mol%, the surface of the thin films displayed contact angles very close to those of pure PTFE, indicating significant hydrophobicity of the surface. Surface analysis of thin films from the PMMA-*r*-TAN copolymers shows that the atomic% of fluorine in the near-surface region roughly twice that in the bulk polymer. This phenomena also occurs in sub-micron fibers electrospun from PMMA-*r*-TAN solutions, in which the surface segregation is similar in magnitude to that measured for the thin films. Extent of surface segregation increases with TAN content, and is marginally improved by annealing. These results demonstrate successful engineering of surface chemistry in electrospun nanofibers, which may be exploited directly in the design of membranes, and demonstrates a pathway for surface functionalization of electrospun fibers for biomedical, composite reinforcement, and other applications.

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