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Electro-spinning of Submicron Polymer Fibers From Poly(tetrahydroperfluorooctyl acrylate-r-methyl methyl methacrylate) Copolymers

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Abstract

Electro-spinning is a process by which sub-micron polymer fibers can be produced with an electrostatically driven jet of polymer solution (or polymer melt). Electro-spun 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 electro-spinning. This has been accomplished by electro-spinning a series of random copolymers of poly(methyl methacrylate (random) tetrahyrdroperflourooctyl acrylate (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 electro-spun 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.

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ELECTRO-SPINNING OF SUBMICRON POLYMER FIBERS FROM POLY(TETRAHYDROPERFLUOROOCTYL ACRYLATE-R-METHYL METHYL METHACRYLATE) COPOLYMERS

1. Introduction

For the past 3 years, interest has grown in a novel fiber production technology know as electro-spinning. Electro-spinning is unique as a fiber-spinning process because of its ability to consistently generate polymer fibers ranging from 50 to 500 nm in diameter [1]. The fibers are formed by an electrostatically driven jet of polymer solution (or polymer melt), as depicted in Figure 1. Polymer solution is forced through a syringe needle at a constant rate, (about 0.5 milliliter per hour [ml/h] in the present case), resulting in the formation of a drop of solution at the tip of the syringe needle. A high voltage (+5 to +15 kv) is applied to the syringe needle, which causes the surface of the drop to distort into the shape of a cone. When a critical voltage is exceeded (typically 5 kv for the solutions discussed in this report), a jet of solution erupts from the apex of the cone. As this jet travels through the air, the solvent evaporates, leaving a polymer fiber to be collected on an electrically grounded target. Because of the small fiber diameters, electro-spun textiles inherently possess a very high specific surface area and small pore size. These properties make electro-spun fabrics interesting candidates for a number of applications including membranes for filtration [2], scaffolding for tissue engineering and other biomedical applications [3], reinforcement in transparent composites [4], and conductive pathways for nano-electronic applications [5].

Most of the recent work [1-7] on electro-spinning has focused on an understanding of the fundamental aspects of the process to gain greater control of fiber morphology and identification of interesting polymer-solvent systems that can be electro-spun. However, little or no effort to control the surface chemistry of electro-spun fibers has been made to date. For many applications, the ability to control the chemistry of the electro-spun fiber surface would greatly improve the overall material performance. For example, electro-spun membranes to be used in breathable garments would benefit from having a fluorinated surface. Such a material would behave in a similar fashion to commercially available (PTFE) membranes that allow perspiration to pass through the garment but prevent the passage of water. Electro-spun fibers with functionalized surfaces and/or chemically specific surfaces would also have a great advantage in biomedical, tissue engineering, and composite applications. Functional surfaces could incorporate anti-bacterial drugs, specific proteins, or resin-coupling agents.

Efforts to control the surface chemistry of organic thin films have been the focus of much research in the last decade [8-11]. The formulation of a non-wetting surface has been of particular interest for solvent-resistant and water-repellent applications. There is a wide variety of these applications that range from car finishes to oil- and stain-resistant textiles and carpets. Because fluorinated homo-polymers are often difficult to process, much effort has been devoted to finding novel methods of obtaining fluorine-enriched polymer surfaces. Some examples of these methods include the use of diblock copolymers, polymers terminated with a fluorinated end cap, and a recent innovative process for coating textiles with fluoro-polymers via supercritical carbon dioxide (Micelle Technology, U.S. Patent 6,030,663).

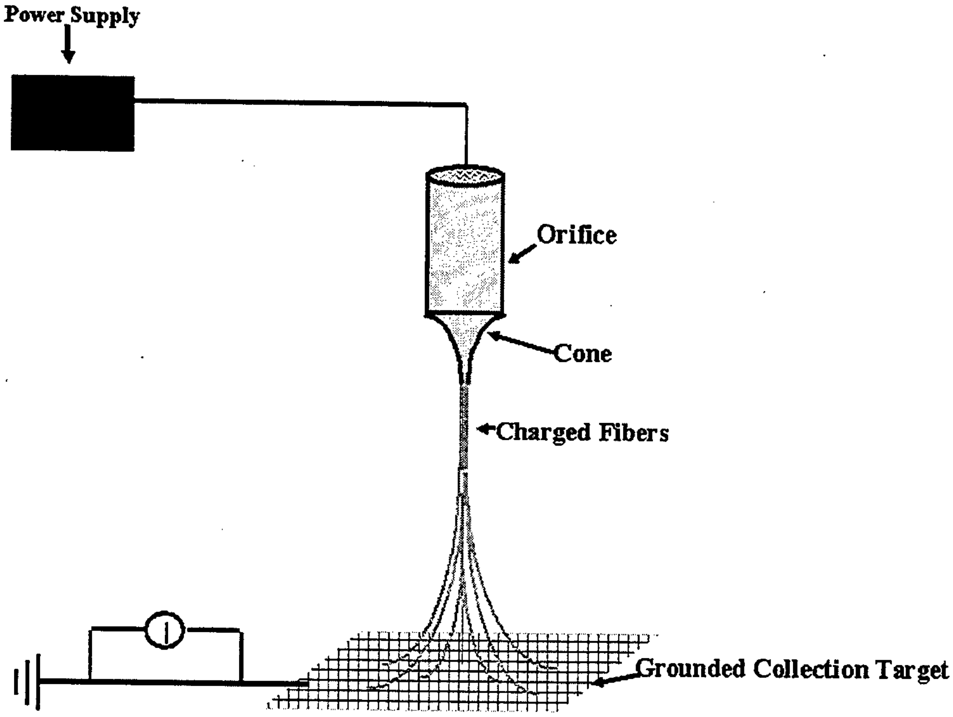

Figure 1. Schematic of Electro-spinning Apparatus.

The work involving diblock copolymers or fluorine-capped homo-polymers is of particular interest to the current work. Typically, scientific investigations of these materials are conducted on spun cast thin films (~100 to 200 nm thickness). The fluorinated chemical moieties have a natural tendency to segregate at the polymer's surface, thereby minimizing the surface free energy of the film at the interface. Annealing of the films above the polymer glass transition temperature may accelerate the process of surface segregation. The goal of the current research is to apply the lessons learned from research about thin films to the process of electro-spinning in order to demonstrate the solution processing of sub-micron fibers with a fluorinated surface.

2. Experimental

The general synthetic route used to produce the copolymers discussed here is illustrated in Figure 2. A series of three poly(methyl methacrylate (random) tetrahyrdroperflourooctyl acrylate (PMMA-r-TAN) copolymers with varying TAN concentrations (3%, 5%, and 10% TAN) and a PMMA homo-polymer were synthesized in the following manner. The monomers were dissolved in 100 ml of toluene with 0.1% wt AIBN (2,2-azobisisobutyronitrile) initiator. The radical polymerization was performed over a period of 24 hours at 70° C (see Figure 2). Galbraith Laboratory performed an independent elemental analysis of the bulk material, which yielded fluorine concentrations indicative of a synthesis taken to 85% completion. Reactivity ratios of similar compounds were examined, which indicated that an alternating copolymer would be preferred to a blocky copolymer structure. The molecular weights for the copolymers and homo-polymer are presented in Table 1.

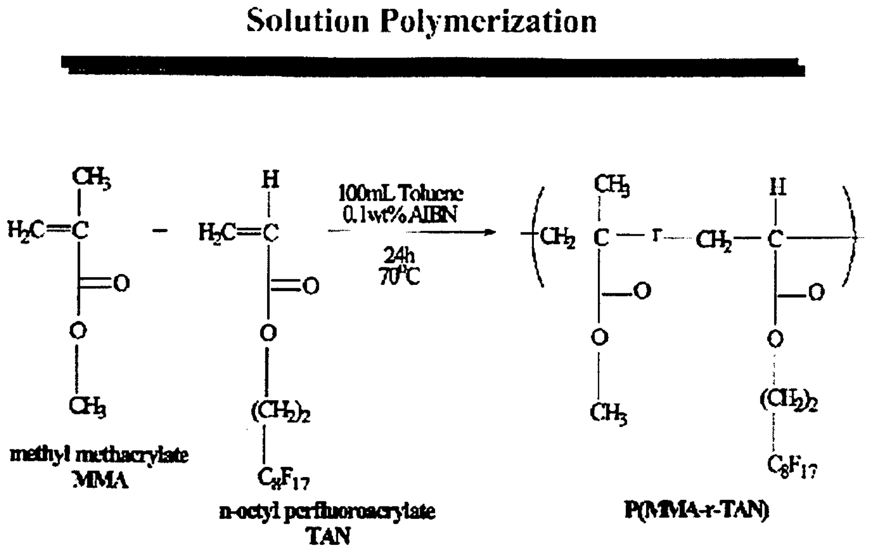

Figure 2. Free Radical Polymerization of PMMA-r-TAN Copolymers.

A series of random copolymer thin films was prepared by spin casting from a toluene solution (5 wt% P[MMA-TAN]) onto solvent-cleaned silicon substrates. Film thickness ranged from 150 nm to 200 nm as determined by X-ray reflectometry. The thin films dried for 18 hours in an ambient temperature vacuum oven. Subsets of these films were then annealed under vacuum at 170° C for 8 hours. Advancing and receding water contact angles were measured for both annealed and unannealed films via an AST[1] Inc. video contact angle (VCA) 2000 system.

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[1] not an acronym

Table 1. Molecular Weight of PMMA Homo-polymer and PMMA-r-TAN Copolymers as Determined by GPC

	Pure PMMA	PMMA-r-TAN 99:1	PMMA-r-TAN 95:5	PMMA-r-TAN 90:10
Molecular Weight (M_w)	159.000	165.000	157,000	155,000
Polydispersity	2.1	1.95	2.1	2.2
Atomic percentage of fluorine	0.2	1.4	8.6	15.6

Fiber mats were electro-spun from solutions of pure PMMA and the random PMMA-TAN copolymer with a ratio of 90% methyl methacrylate (MMA) monomer units to 10% TAN units. The materials were dissolved in a binary solvent that contained 10% dimethyl formamide and 90% toluene by volume. The polymer concentration of these solutions was 10% by weight. Polymer solution was fed at a rate of about 1 ml/h through a stainless steel syringe pipette needle (18 gauge) that carries a potential bias of +5 kv. The syringe is placed vertically 4 inches above an electrically grounded aluminum plate upon which the fibers are collected. The resulting fiber mats were then annealed at 120° C for a period of 4 hours under vacuum.

Micrographs of the electro-spun materials were obtained with a Phillips-Electroscan environmental scanning electron microscope. A sample was mounted on a piece of copper tape attached to a standard sample stub. Images of the samples were obtained at a working distance of 9 mm in a water vapor atmosphere at room temperature and at a 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 electro-spun fiber samples was performed with a Kratos Axis 165 X-ray photoelectron spectroscopy system, equipped with a hemispherical analyzer, which characterized the near surface composition of the thin films. A 100-w monochromatic Al Kα (1486.7 electron volts [eV]) beam irradiated a 1-mm by 0.5-mm spot. All spectra were taken at a 2- by 10^{-9}-torr vacuum environment. Survey and elemental high resolution scans for C_{1s}, F_{1s}, and O_{1s} were taken at pass energy = 80 eV for 5 minutes and pass energy = 40 eV for 2 to 8 minutes, depending on S/N, respectively. The photo-emission spectra allow quantitative (surface concentrations) and qualitative (functional group identification) information to be obtained.

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 being examined. TAN has a photo-emission cross section 4 times that of C^{14}, resulting in increased charging observed with the increased TAN incorporation. Saturated hydrocarbon C1s in the spectra were shifted by a correction factor (±•) to C_{1s} BE = 285.0 eV.

3. Results and Discussion

The model system chosen for this work was a novel random copolymer of MMA and TAN. This material has an advantage over diblock copolymers and fluorinated end-capped homo-polymers that are usually employed in surface segregation studies. Both the diblock copolymers and the end-capped polymers are made through complicated synthesis routes. As a result, the cost of these materials is high, which increases the cost of the final product. In contrast, the random copolymers used in this study were made with a single-step free radical polymerization. Some previous work **[10,11]** focused on the surface segregation of fluorine in thin films cast from low molecular weight random copolymers (6,000 megawatts [MW]) that were synthesized via a radical polymerization. To our knowledge, this work is the first to demonstrate that high molecular weight random copolymers show significant enrichment of fluorine at the interface of a thin film surface and air.

3.1 Thin Films

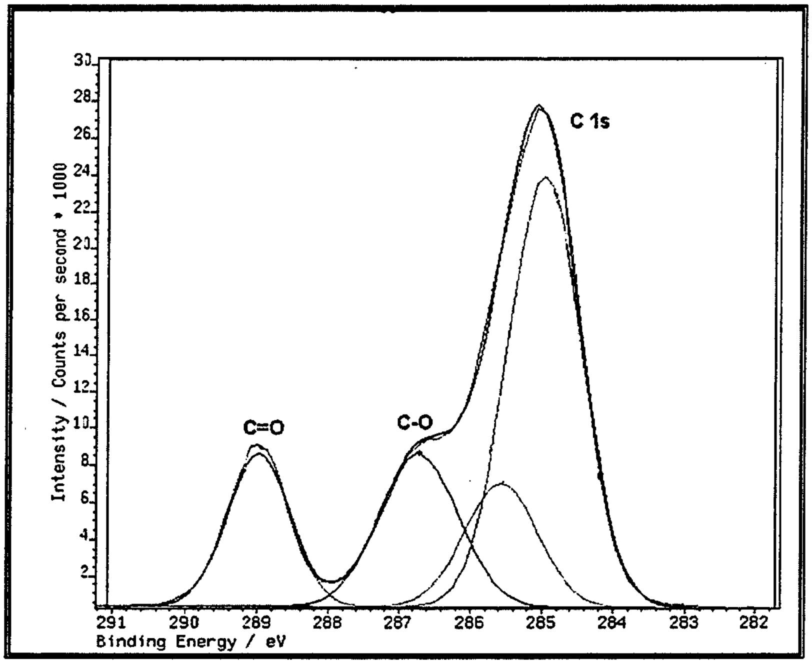
The as-spun thin films were analyzed with advancing and receding contact angle measurements for a water drop. The advancing contact angles were observed to increase from 76° for pure PMMA to 103° for the 90:10 P(MMA-r-TAN) copolymer. These films were then annealed under vacuum at 170° C for 8 hours, and the contact angle measurements were repeated. All contact angle values are reported in Table 2. A slight increase in the contact angle was observed for the P(MMA-r-TAN) copolymers (TAN). The hydrophobic response observed through contact angle measurements indicates increasing fluorine surface segregation with increasing TAN content and that segregation is improved slightly upon annealing. A contact angle of 107° was measured for a thin film spun cast from 90:10 P(MMA-TAN) polymer solution. This compares favorably with contact angle measurements for pure poly(tetrafluoroethylene) surfaces (108° to 112°), which indicate a high degree of fluorine segregation at the film surface resulting from a relatively small amount of fluorinated monomer incorporated into a random copolymer. The data also indicate that there is a significant difference between the advancing and receding contact angles for the thin films. A possible explanation for this contact angle hysteresis is presence of chemical heterogeneity at the film surface. It is likely that the fluorinated moieties exist in small domains that are interspersed with large hydrocarbon moieties **[10,11]**. Other factors, such as surface roughness and the tendency of the fluorinated side chains to try to bury themselves in the presence of water **[13]** might also contribute to the contact angle hysteresis.

Table 2. Water Contact Angles for As-Cast and Annealed Films

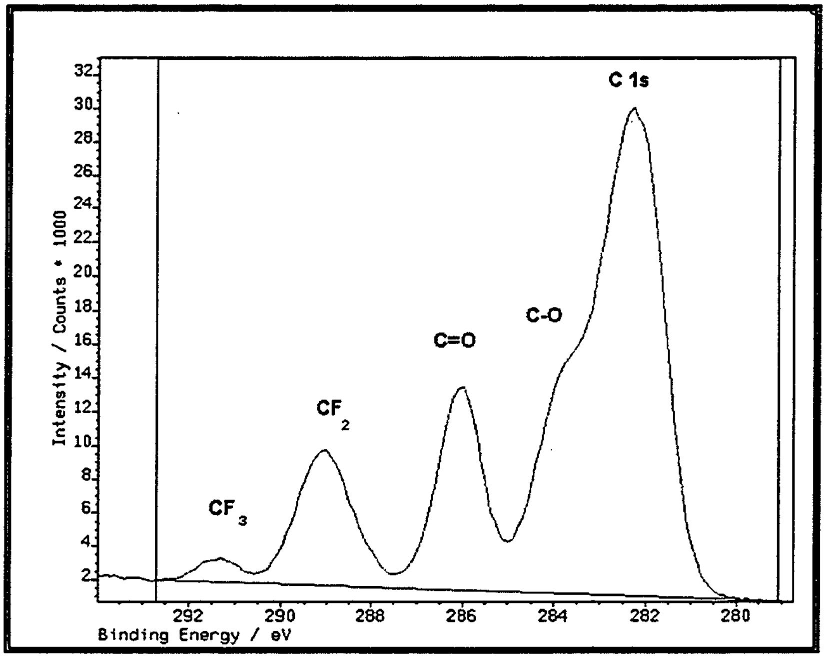
	Pure PMMA (degrees)	99/1 (degrees)	95/5 (degrees)	90/10 (degrees)
Unannealed				
Advancing	76	80	92	103
Receding	67	68	68	73
Hysterisis	9	12	24	30
Annealed				
Advancing	76	87	98	107
Receding	68	71	80	82
Hysterisis	10	16	18	25

The contact angle experiments indicate that a significant number of the fluorinated side chains in the random copolymer have bloomed to the air interface, creating a hydrophobic surface. 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 the fluorinated (09:10 P(MMA/TAN) and non-fluorinated methyl methacrylate (PMMA) films are shown in Figure 3. These spectra clearly show the distinct photoelectron signature of each material. Poly(methyl methacrylate) has four functional species that contribute to the total C_1s peak: C-C (285 eV), C-C b-shifted (286.2 eV), C-O (286.8 eV), and the O=C-O (289.4 eV). In the TAN polymers, two more peaks resulting from the CF_2 and CF_3 bonds are evident. Both the PMMA homopolymer and the fluorinated copolymers produced spectral peaks corresponding to the oxygen moieties, and the copolymers had a single peak corresponding to the fluorine moiety (not shown). In both cases, the O_1s peak is comprised of two distinct peaks corresponding to O-C And O=C. No unexpected elements were detected.

After appropriate linear background subtraction, the total C, O, and F were quantified through an integration subroutine with the manufacturer's peak-fitting software. Analysis demonstrated that the peak intensities were consistent with the atomic structure of the MMA and TAN units. 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 [14]. The individual peak fits agreed well with the expected structure and stoichiometry of the MMA-TAN systems.



a. PMMA homo-polymer



b. 90/10 PMMA-r-TAN copolymer

Figure 3. X-ray Photoelectron Spectroscopy Carbon Spectra Obtained From Electro-spun Fiber Mats.

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 percent concentration of a given chemical moiety in the near surface region (~3 nm depth) of a film or fiber from the XPS data. These data are presented in Figure 4, which shows a series of plots of the atomic percent of fluorine as a function of the TAN content of the copolymer in the bulk, thin film and fiber forms. The solid line, A, in Figure 4 is the atomic percent fluorine as a function of TAN content of the copolymers in the bulk form as determined by elemental analysis. When this is compared to the data (dashed line, B, in Figure 4) obtained from the XPS experiments on the copolymer thin films, it is seen that the fluorine content in the near surface region of the thin films is approximately double that found for the bulk measurement. These results agree very well with the contact angle measurement data, which indicate that the fluorinated segments of the random copolymer readily segregate at the film-air interface.

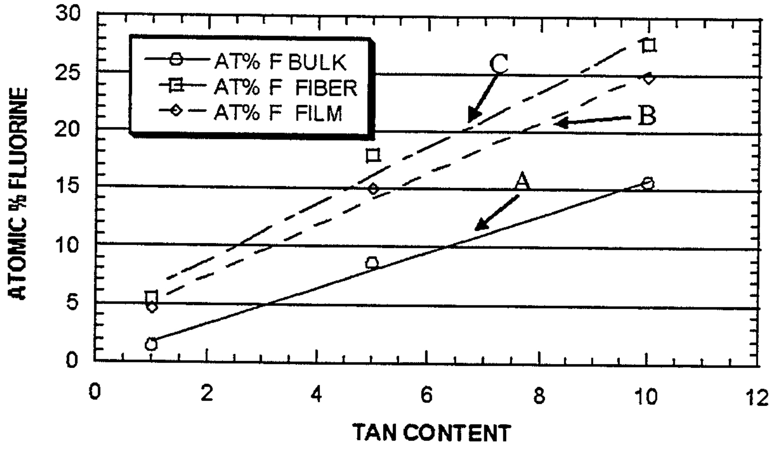
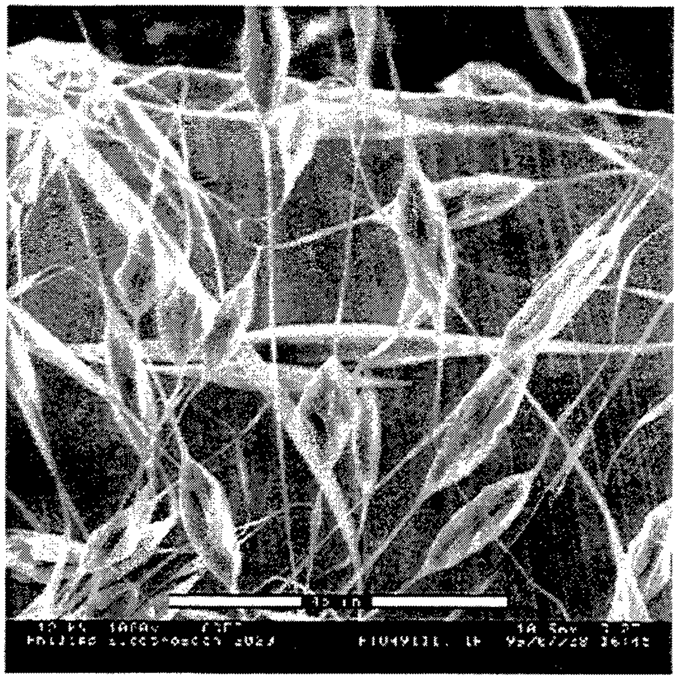


Figure 4. Atomic Percent Content of Fluorine as a Function of TAN Content.

3.2 Electro-spun Fiber Mats

Having proved the feasibility of obtaining a hydrophobic surface via a high molecular weight random copolymer, the authors electro-spun fibers of each of the random copolymers and the homo-polymer control from a solvent mixture of 10%(wt) dimethyl formamide and toluene. Figure 5 shows electron micrographs of fibers electro-spun from solutions of pure PMMA and 90/10 copolymer. The fiber diameters in each of the pictures range from 2 microns to 300 nm, which was typical for all samples examined and within the expected range for electro-spun fibers. An interesting feature in all the electro-spun samples examined was the bead morphology along the length of the fibers. All the beads in these samples have a wrinkled, raisin-like surface texture that is different from the typical smooth sphere or oval that has been reported in the past [1,3,6,12].

a. PMMA homo-polymer



b. PMMA-r-PTAN copolymer

Figure 5. Electron Micrographs of Electro-spun Fibers.

The presence of the bead morphology in electro-spun samples has been well documented [1,3,6,12]. The formation of the beads is thought to occur when processing parameters such as solution viscosity, solution charge density, spinning voltage, and solution feed rate are not properly optimized. This results in an imbalance among the three major forces (electrostatic force, visco-elastic force, and surface tension) acting on the jet. This condition favors the formation of a varicose instability and the jet starts to disintegrate into drops [13]. As the solvent evaporates, the visco-elastic response of the polymer solution stabilizes the jet just before disintegration, resulting in a string of beads connected by thin fibers. A possible explanation for the wrinkled texture of the beads in Figure 5 is that rapid evaporation of the solvent caused a skin to form at the surface of the beads, while the liquid center continued to be drawn out during the formation of the connecting fibers. As solution is removed from the center of the bead, the outer skin collapses, leaving the wrinkled bead.

The electro-spun samples of the three copolymers were annealed for 4 hours at 120° C. XPS analysis was then performed and the atomic percent of fluorine in the near surface region was determined for each sample. The results are represented by line C in Figure 4. As determined from the data obtained from the thin films, the atomic percent of fluorine in the near surface region of the electro-spun fibers is roughly double the amount of fluorine in the bulk samples. This is clear evidence that the fluorinated side chains have segregated to the surface of the electro-spun fibers. Additionally, it can be seen that the fluorine content measured for the fiber mats was 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).

4. Conclusions

It has been demonstrated that it is possible to obtain significant segregation of fluorine at the surface of thin films of high molecular weight, fluorinated random copolymers. Sub-micron fibers with fluorinated surfaces have been produced by electro-spinning random copolymer solutions. XPS analysis of fiber mats electro-spun from a series of random copolymers of PMMA-r-TAN shows that the atomic percent of fluorine in the near surface region of the electro-spun fibers is roughly twice the value in a bulk sample, as determined through elemental analysis. This result is in good agreement with XPS results obtained from thin films of the same copolymers.

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13. ABSTRACT *(Maximum 200 words)*

Electro-spinning is a process by which sub-micron polymer fibers can be produced with an electrostatically driven jet of polymer solution (or polymer melt). Electro-spun 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 electro-spinning. This has been accomplished by electro-spinning a series of random copolymers of poly(methyl methacrylate (random) tetrahyrdroperflourooctyl acrylate (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 electro-spun 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.

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