Electrospinning Superhydrophobic Fibres Using Surface Segregating End-Functionalized Polymer Additives

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ABSTRACT: We describe here a facile route for the *in situ* modification of the surface properties of fibres produced by electrospinning polystyrene containing small quantities of compatible polymer additives, end functionalized with 1-3 fluoroalkyl groups. Such additives undergo spontaneous surface segregation during the electrospinning process resulting in fibres with low surface energy, fluorine rich, superhydrophobic surfaces. Surface properties were analyzed using static contact angle measurements (with water as the contact fluid) and X-ray photoelectron spectroscopy. We report the effect of a number of parameters on the surface properties of the resulting polystyrene fibres including the molecular weight and concentration of functionalized additive, the number of fluoroalkyl groups, the effect of annealing and spinning solvent. The majority of the fibres were successfully produced using THF as the spinning solvent and fibres with a contact angle of approximately 150 degrees were attainable. However, preliminary investigations using a blend of polystyrene and 4% by weight of such an additive, end-functionalized with 3 C_8F_{17} group in a mixed solvent of DMF/THF (3:1 v/v) resulted in a mat of fibres with a superhydrophobic surface and a contact angle of 158 degrees.

Introduction

Electrospinning is an area of intense academic activity and is emerging as a technique of significant industrial interest for applications as diverse as optoelectronics, sensor technology, catalysis, filtration, and medicine[1-5]. Electrospinning is an extraordinarily versatile, almost generic technique for producing fibres with diameters ranging from microns to nanometres, from virtually any soluble polymer; those polymers which are intractable can be electrospun from the melt. It is possible to electrospin homopolymers, copolymers, polymer blends and polymer composites, however whilst electrospinning appears to be straightforward it is in reality a rather complicated process whose success depends on a balance of molecular, process, and technical parameters. All of these factors play a major role in fibre formation and resulting fibre morphology can vary enormously[1]. The desired morphology is for uniformly round fibres but on occasion beaded fibres (resembling a pearl necklace) or flat ribbon like fibres are formed; in some cases fibres are not produced at all and beads/particles result.

The production of surface functionalized fibres has been described in the literature. Several approaches have been successfully used to modify electrospun nanofibers, such as electrostatic surface coating,[6,7] physical or chemical vapour deposition[8-10] plasma treatments[11-13] and coaxial electrospinning[14], though all these methods except coaxial spinning involve a post-spinning process and all or most of these approaches tend to suffer from (at least one of) safety hazards, being expensive or restricted to batch processing. However, in situ surface functionalization during the spinning process, through the spontaneous surface segregation of functionalized additives provides a facile and attractive alternative to the methods described above and is a strategy that has not been widely investigated. Reports in the literature of fluorinated additives and fluorine containing polymers being used to create low surface energy properties in polymer thin films are not uncommon. Surface adsorption is spontaneous if there is an accompanying reduction in the surface energy and it is relatively straightforward to increase the hydrophobicity of polymer surfaces by the use of polymers functionalized with low surface energy fluorocarbon (CF) groups. We have recently shown in situ surface segregation to be a particularly effective approach for the surface functionalization of polymer thin films when relatively low molecular weight polymers carrying 2-4 CF groups at their chain-end are used as additives in low concentration[15-19]. Moreover, PTFE-like surface properties were achieved with as little as 0.1 wt % of an additive carrying 3 C_8F_{17} groups.

There have also been many notable examples describing the production of low energy/hydrophobic surfaces by electrospinning/electrospraying polymers. Jiang et al[20] electrospun polystyrene from DMF/THF to give a fibre mat with contact angles of 139.1 degrees and went on to spin/spray a dilute solution of polystyrene to give a film of porous microparticles which gave a water contact angle of 162 degrees. This superhydrophobicity arises predominantly as a result of surface roughness and it was noted that this surface, although hydrophobic, was unstable. A more stable surface film structure was obtained by spinning a 7% solution of polystyrene which yielded a hybrid structure of beaded fibres, with a network of fibres of diameter 60-140 nm and microparticles of diameter 3-7 microns. Acatay[21] used a fluorinated comonomer, present at up to 50 wt % to achieve superhydrophobic surfaces via an electrospinning process. They electrospun a thermosetting polymer using a copolymer of acrylonitrile and α,α-dimethyl meta-isopropenylbenzyl isocyanate and 50 wt % of a perfluorinated diol. The resulting surfaces were a mixture of fibres and beaded fibres and maximum contact angles were achieved for a heavily beaded surface produced by the spinning of a low viscosity (low molecular weight) polymer – thereby achieving hydrophobicity via a combination of surface roughness and the use of a low surface energy comomomer. Ma[22] describes low surface energy fibres produced by electrospinning polystyrene – polydimethylsiloxane block copolymers which were contaminated with polystyrene homopolymer (arising from the block copolymer synthesis). The actual composition of the polymer was 77% block copolymer and 23% polystyrene homopolymer, and the volume fraction of siloxane in this blend was

43%. Unsurprisingly, this relatively high content of low surface energy siloxane polymer resulted in fibres which gave water contact angles of up to 163 degrees. Although the low surface energy component undoubtedly contributes to the creation of superhydrophobic surface properties, it is questionable whether such effects could be achieved with low concentrations of this block copolymer in a matrix. Analogous work[23] describing the use of fluorinated block copolymers to modify the surface properties of polymer films noted that the when such block copolymers are used at additive levels (low concentrations), successful surface modification relies on surface migration of the block copolymer to the air-polymer interface and the kinetics of surface segregation comes into play. Self-organization of the additive block copolymers in the bulk is unavoidable and significantly retards surface segregation. It was reported that even annealing the films for several hours at 150°C was not enough to allow diffusion of the block copolymers from the bulk to the surface to give uniform coverage. The use of low surface energy block copolymers to surface modify fibres produced by electrospinning will be subject to the same limitations. The potential problems associated with electrospinning block copolymers was further demonstrated by Valtola[24] who synthesised (by atom transfer radical polymerisation) low molecular weight block copolymers ($M_n < 15{,}000$ gmol^{-1}) in which one block was polystyrene and the other block comprised of one of four fluorinated monomers. The molecular weight, composition and choice of fluorinated monomer was varied but in all cases a combination of the low molecular weight and the tendency of the copolymers to aggregate resulted in the formation of 10-20 μm particles rather than fibres, although contact angles in some cases exceeded 150 degrees. Furthermore, recently a functional perfluorinated block copolymer[25] was used to coat the surface of aluminium substrates by electrospinning, although the resulting surface was very heterogeneous in morphology and defined fibres were not produced.

Although the above described systems often result in superhydrophobic surfaces, in the main the surfaces are heterogeneous in morphology rather than uniform fibres and there are many specific applications which require the use of fibres rather than beads. Due to their high surface area, electrospun nanofiber mats are highly effective as sensors, as filters and a growing number of researchers are using electrospun nanofiber mats as scaffolds for culturing cells[26] – thus the simultaneous control of fibre morphology as well as surface property is highly desirable.

The use of surface segregation as a strategy to modify surface properties of electrospun fibres has been demonstrated in a small number of examples. Spontak[27] described the field driven surface segregation of a polymer-peptide conjugate during electrospinning and demonstrated that the peptide segment selectively adsorbed at the air polymer interface. Börner[28] *et al* similarly used a single-step process to produce poly(lactic-co-glycolic acid) (PLGA) nanofiber meshes with surfaces enriched with biofunctional peptide by spinning a homogeneous mixture of PLGA and a polymer-peptide conjugate (poly(lactic acid)-block-CGGRGDS). Bianco *et al*[29] spun polyamide 6 nanofibres in the presence of a fluorinated acridine and found that with the addition of increasing amounts of the acridine (1-6 wt%), static contact angles with water (as the contact fluid) on the fibres increased progressively from 61 degrees for unmodified polyamide to 123 degrees for the polyamide fibres doped with 6% acridine. Moreover, Long *et al*[30,31] produced hydrophobic fibres by electrospinning poly(methyl methacrylate) containing up to 10 wt % of a low molecular weight ($M_n \sim 1600$ gmol^{-1}), hyperbranched, end perfluorinated and alkylated polyethyleneimine additive (PFA). It was noted that the fluorinated additive selectively segregated to the fibre surface with the amount of fluorine at the surface (determined by X-ray photoelectron spectroscopy) depending primarily upon additive concentration. It was also reported that the presence of additive in solution suppressed beaded fibre formation at low PMMA solution concentrations.

In contrast to the previously reported work, the aim of the current research was to produce low surface energy, superhydrophobic fibres (as opposed to beads or beaded fibres) with stable/durable surface properties through the use of low concentrations (less than 10%) of a surface segregating, surface modifying additive. In this way, the bulk (mechanical) properties of the fibre can be controlled by the choice of matrix polymer whilst the surface properties are managed by the addition of the functionalised additive. Moreover, if the additive is sufficiently surface-active to migrate to the surface during the spinning process, the need for a potentially expensive post-spinning process is avoided. Such an approach has advantages in not only cost but allows the surface and bulk properties to be tailored independently. Furthermore, our experience of using analogous additives in the production of surface modified thin films shows that these end-functionalised polymer additives are compatible with the bulk (up to about 10 wt %) and do not aggregate at these concentrations. As such they are not subject to the same limitations that are associated with block copolymers.

Durability of properties at a modified surface is an inevitable concern since this potentially places limitations on the range of applications and product lifetime and whilst the work of Long[29,30] and Bianco[28] showed unequivocally that spontaneous surface segregation of low surface energy additives can be achieved during the electrospinning process, the use of such low molecular weight additives is unlikely to result in a long term, durable, fluorinated surface layer – such small molecules are susceptible to surface erosion through environmental wear and tear. Clearly the strength of the interaction between the modified surface and the bulk material is of critical importance to its durability and the use of a polymeric additive, capable of chain entanglement with the bulk sub-phase is expected to enhance durability and this effect is the subject of ongoing studies.

Thus we report here, the electrospinning of polystyrene fibres in the presence of a series of fluoroalkyl end-functionalized polystyrene additives, with molecular weights in the range of 6,000– 25,000 $gmol^{-1}$ and with 1 to 3 C_8F_{17} fluoroalkyl (CF) groups. These additives undergo spontaneous surface segregation during the electrospinning process and we report the results of investigations into the relationship between molecular weight, concentration and number of CF groups of each additive and the surface properties of the resulting fibres. Surface properties were measured by static contact angles (with water as the contact fluid) and X-ray photoelectron spectroscopy. Furthermore, the results of enhanced surface segregation achieved by post-spinning annealing at the onset of the glass transition temperature of polystyrene are discussed.

Experimental Section

Materials. Benzene (HPLC grade), toluene (HPLC grade), styrene, hexane (HPLC grade) and cyclohexane (HPLC grade) (all Aldrich) were purified, dried and degassed by freeze/thaw cycles over calcium hydride, CaH_2 (Aldrich). sec-Butyllithium (sec-BuLi) 1.4 M in cyclohexane, 1H,1H,2H,2H-perfluorodecyldimethyl chlorosilane (reagent grade, 98%) 3,5-di-t-butyl-4,4-hydroxytoluene (BHT) (99%), 3,5-dihydroxybenzyl alcohol (99%), anhydrous potassium carbonate (99.995%), 18-crown-6 (99%), carbon tetrabromide (99%), triphenylphosphine (99%) (all Aldrich) and 3-(perfluorooctyl)propanol (Fluorochem) were used as received. Tetrahydrofuran (THF, Aldrich), was purified over Na/benzophenone until purple color that developed remained. 3,5-(di-3-(perfluorooctyl)propyloxy)benzyl bromide and 3,4,5-(tri-3-(perfluorooctyl)propyloxy)benzyl bromide were prepared according to previously described methods[17]. Dimethylformamide (DMF) (99%, Aldrich) and THF (99%, Aldrich) for electrospinning were used as received.

Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity and light scattering detectors. A value of 0.185 (obtained from Viscotek) was used for the dn/dc of polystyrene. 2 x 300 mm PLgel 5µm mixed C columns were used with a linear range of molecular weight from 200 to 2,000,000 g/mol; THF was used as the eluent with a flow rate of 1.0mL/min at 35 ºC.

1H NMR analysis was carried out on a Varian VNMRS 700 MHz and Bruker Avance-400 MHz spectrometer using CDCl3 as a solvent. Spectra were referenced to the trace of CHCl3 (7.3 ppm) present in the $CDCl_3$.

The electrospun fibres were examined by Environmental Scanning Electron Microscopy (ESEM); the fibres were imaged uncoated using a Philips/Fei XL30 ESEM fitted with a turbomolecular pump and the images were obtained using an annular, on-axis back-scattered electron detector, with a sample-chamber water-vapour pressure of 0.5 Torr +/- 0.1 Torr and an accelerating voltage of 15kV.

Static contact angle measurements were carried out using a Rame-Hart goniometer model 100-00-230.

Glass transition temperatures were measured by differential scanning calorimetry (DSC) using a TA Instruments Q1000 DSC.

X-ray photoelectron spectroscopy analysis was carried out using a Kratos AXIS ULTRA with a monochromated Al kα X-ray source (1486.6eV) typically operated at 10mA emission current and 12kV anode potential. The take off angle for the photoelectron analyzer was 90 degrees.

Polystyrene. The syntheses of polystyrene matrix samples for electrospinning were carried out using standard high-vacuum techniques at room temperature with benzene as the solvent and *sec*-butyllithium as the initiator – the details of such polymerizations have been described elsewhere[32]. Three samples of polystyrene were prepared, PS80, PS235 and PS525 with molar masses of 80,000 gmol^{-1}, 235,000 mol^{-1} and 525,000gmol^{-1} respectively.

Fluoroalkyl end capped Polystyrene. The synthesis of samples of fluoroalkyl end-capped polystyrene with a variety of molecular weights was achieved by the controlled termination of polystyrene – prepared by living anionic polymerization – with one of three end capping agents; 1H,1H,2H,2H-perfluorodecyldimethyl chlorosilane (1CF), 3,5-(di-3-(perfluorooctyl)propyloxy)benzyl bromide (2CF) or 3,4,5-(tri-3-(perfluorooctyl)propyloxy)benzyl bromide (3CF) according to previously described reports[33,34].

Electrospinning Conditions. Optimal conditions for electrospinning polystyrene fibres were obtained by varying the following parameters; polymer matrix molecular weight (PS80, PS235 and PS525), solution concentration (15 to 35% w/v), feed rate (5, 10, 15, and 20 ml per hour) and voltage (10, 15 and 20kV). The needle to tip collector distance (NCD) was 25cm and a 10ml PTFE Luer lock syringe (Hamilton, 1000-Series Gastight, 1010) fitted with a 0.838mm inside diameter, blunt needle (Sigma Aldrich, 316-SS stainless steel syringe needle, blunt tip, 18G x 2in long Luer hub) was used.

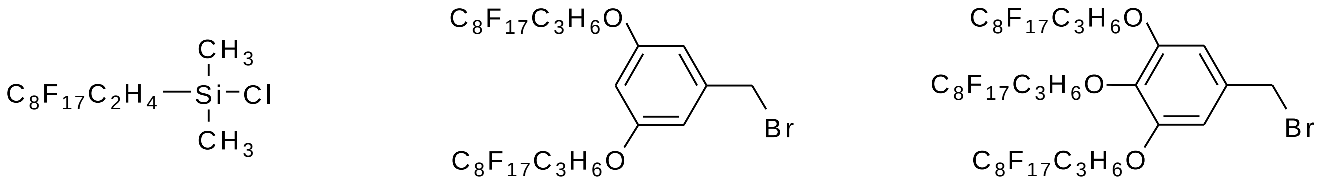
Electrospinning polystyrene with additives. THF. Mixtures of matrix polystyrene (525,000 gmol^{-1}) and polystyrene additive with compositions containing up to 10% by weight of additive were dissolved in THF to give a total concentration of 20% w/v. Feed rates of 5mlh^{-1} and a voltage of 10-20kV were used for the electrospinning.

DMF/THF. Mixtures of matrix polystyrene (235,000 gmol^{-1}) and polystyrene additive with compositions containing up to 10% by weight of additive were dissolved in DMF/THF (3:1 v/v) to give a total solution concentration of 30% w/v. Feed rates of 5mlh^{-1} and a voltage of 20kV were used for the electrospinning.

Annealing. Electrospun fibre mats were annealed in a vacuum oven at 100^{o} C – the temperature corresponding to onset of the glass transition temperature of the fibres (as determined by DSC) – for up to 2 weeks. Samples were removed for contact angle measurements (with water as the contact fluid) after 1 day, 2 days, 4 days, 1 week and 2 weeks.

Results and Discussion

A series of fluoroalkyl end functionalized polymers have been prepared by end-capping polystyrene prepared by living anionic polymerization via a controlled termination reaction. A full discussion of the synthesis of both the end groups and the functionalized polymers has recently been described elsewhere[34]. Three end capping agents (figure 1) have been used which introduce 1, 2 or 3 fluoroalkyl groups onto the chain end of polystyrene to yield polymer additives denoted PS1CF, PS2CF and PS3CF respectively.



I CF **2 CF** **3 CF**

Figure 1. End capping agents with 1, 2 and 3 fluoroalkyl groups used in the synthesis of end functionalized polystyrene

Polystyrene additives with molecular weights varying from 6,000 – 25,000 gmol^{-1} were prepared and the molecular weight, number of end groups and extent of end-capping for all of the polymer additives (and matrix polymers) used in this study are detailed in table S1 (electronic supporting information). Throughout this report we will refer to the various functionalized additives using the following nomenclature – PSXCFYK where PS refers to polystyrene, XCF denotes the number of CF groups and

YK refers to molar mass of the additive. Thus PS3CF10K is a polystyrene additive with 3 CF groups and a molar mass of approximately 10,000 $gmol^{-1}$. Detailed molecular weight data is included as electronic supporting information.

Electrospinning from THF. Although electrospinning is a relatively facile and versatile method for producing polymer fibres with diameters in the micron to nanometer range, there is a wide range of experimental parameters that must be considered in order to optimize the spinning process. Discussion of the optimization of the spinning process from THF is included as electronic supporting information.

Mixtures of a polystyrene matrix PS525 (M_w 525,000 $gmol^{-1}$) and each of the five fluoroalkyl end functionalized polystyrene additives (see table S1) were co-dissolved in THF such that the total concentration of polymer was 25% w/v. Solutions were prepared containing each functionalized additive at 6 different concentrations with respect to the matrix polymer PS525; 1%, 2%, 3%, 4%, 8% and 10%. Although the addition of up to 10% by weight of the low molecular weight additives to PS525 will have altered the rheological properties and surface tension of the polymer solution, the addition of the fluorinated additives did not have a deleterious effect upon the electrospinning process. At a polymer solution concentration of 25% w/v, ribbon-like fibres were consistently obtained with very similar dimensions to those shown in figure S1C (electronic supporting information).

Electrospinning from DMF/THF (3:1 v/v).

Electrospinning polystyrene from THF resulted in ribbon like fibres with a distribution of fibre sizes in the 10s of microns. It has been noted previously that in electrospinning polystyrene, the use of low volatility solvents with high dielectric constants, such as DMF can result in more uniform fibres[35,36]. Moreover, it has also been reported that mixtures of DMF and THF can lead to further improvements beyond that of either DMF or THF alone[37]. Preliminary experiments have been carried out to produce thinner and more uniform fibres using a blend of DMF/THF (3:1 v/v) as the spinning solvent and the impact of this finer and more uniform fibre structure on the surface properties of functionalized fibres investigated. Following a series of optimization spinning experiments it was found that PS235K was sufficiently high molecular weight for the matrix polymer and a 30% w/v solution of this polymer in the

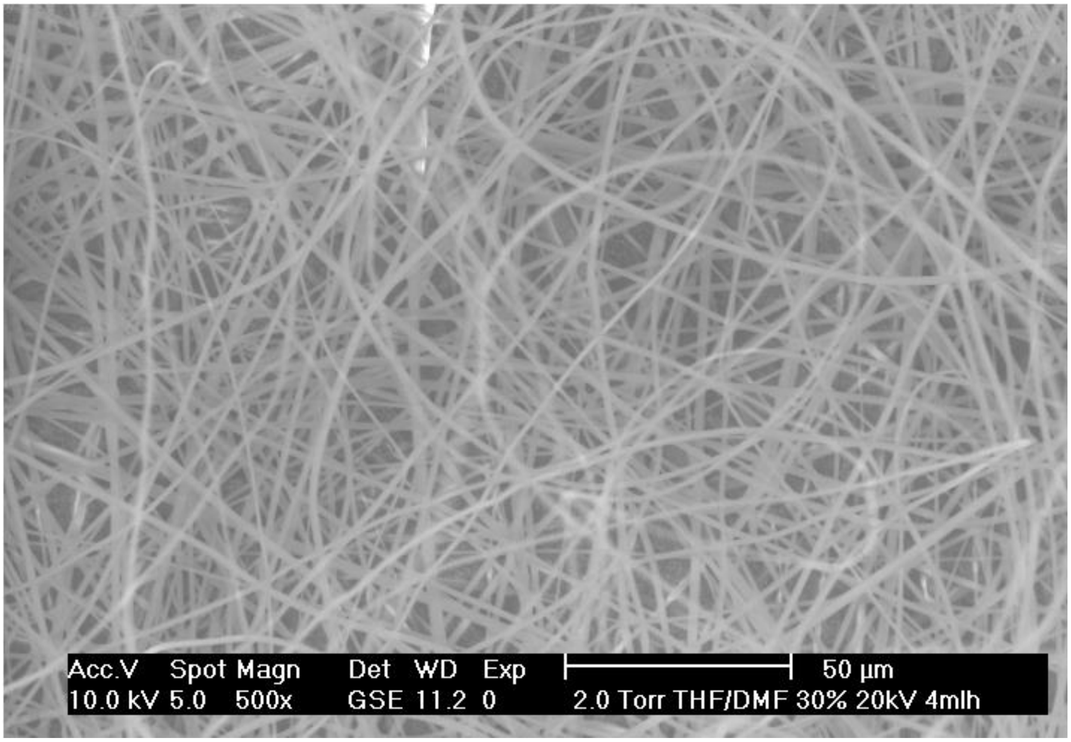


Figure 2. ESEM image of PS235 fibers electrospun from DMF/THF (3:1) solution at a concentration of 30% w/v with a feed rate of 4mlh-1 and voltage of 20kV.

mixed solvent was spun using a voltage of 20kV and much slower feed rates (4-6mlh^{-1}) than for pure THF. The resulting fibres were cylindrical (rather than ribbon like), much more uniform and much smaller in fibre diameter; the average fibre diameter when using the mixed solvent was 1-2 microns, more than an order of magnitude smaller than when using THF as the spinning solvent – see figure 2

Contact Angle Measurements of Fibres spun from THF

The principal objective of this work was to ascertain the extent to which fluoroalkyl end functionalized polymer additives could undergo spontaneous surface segregation *during* the lifetime of the electrospinning process resulting in efficient *in-situ* modification of the surface properties of the resulting fibres. Although a small number of previous studies have shown that low molecular weight fluorinated additives do successfully migrate to the surface during the electrospinning process [29,30], to the best of our knowledge this is the first report of low surface energy polymeric additives being used for this purpose. We have recently shown [15-19,34] that polymeric fluoroalkyl additives with molecular weights as high as 40,000 gmol^{-1} are able to successfully surface segregate in thin films, although somewhat unsurprisingly, lower molecular additives and additives with a higher fluorine contact are more effective at generating significant changes in surface properties. Spontaneous surface segregation – driven by a reduction in surface energy - was shown to be an extremely efficient process and in some cases it was possible to generate poly(tetrafluoroethylene)-like surface properties during the spin coating of a polymer film containing substantially less that 1% (by weight) of additive [17]. In order to investigate the extent to which this behaviour could be replicated during the electrospinning process, static contact angle measurements using water as the contact fluid were carried out on mats of the electrospun fibres containing various concentrations (0-10%) of fluorinated additives. Contact angle measurements on thin films can produce variable results with errors of +/- 1-2 degrees. Contact angle measurements on mats of electrospun fibres show two general and striking differences to similar measurements in thin films prepared by spin coating. Firstly, contact angles on mats of electrospun fibres show greater variation/errors (up to +/- 4 or 5 degrees) due to the inherent heterogeneity of the fibre mats and therefore to maximize confidence in our results, all the data quoted here are the average of at least 6 (usually more) separate measurements. In some cases, the comparative differences in contact angle under discussion are modest and the errors associated with contact angle analysis should not be ignored. A full statistical analysis of all the contact angle data has been carried out and the standard deviation for any individual data point varies from approximately 2.0 to 4.0 in a few extreme cases but in the majority of cases varies between 2.5 and 3.5. However to display error bars on each data point would unnecessarily clutter the figures – thus, an error bar representing a typical standard deviation of 3.0 has been added to each figure for illustrative purposes. Although the error in any given data point is in some cases comparable to the difference between data sets, we are confident that the trends observed are genuine and reproducible. The second difference is that the contact angles are generally much higher than those observed on thin films. A mat of fibres spun from pure PS525 (no additive) has a contact

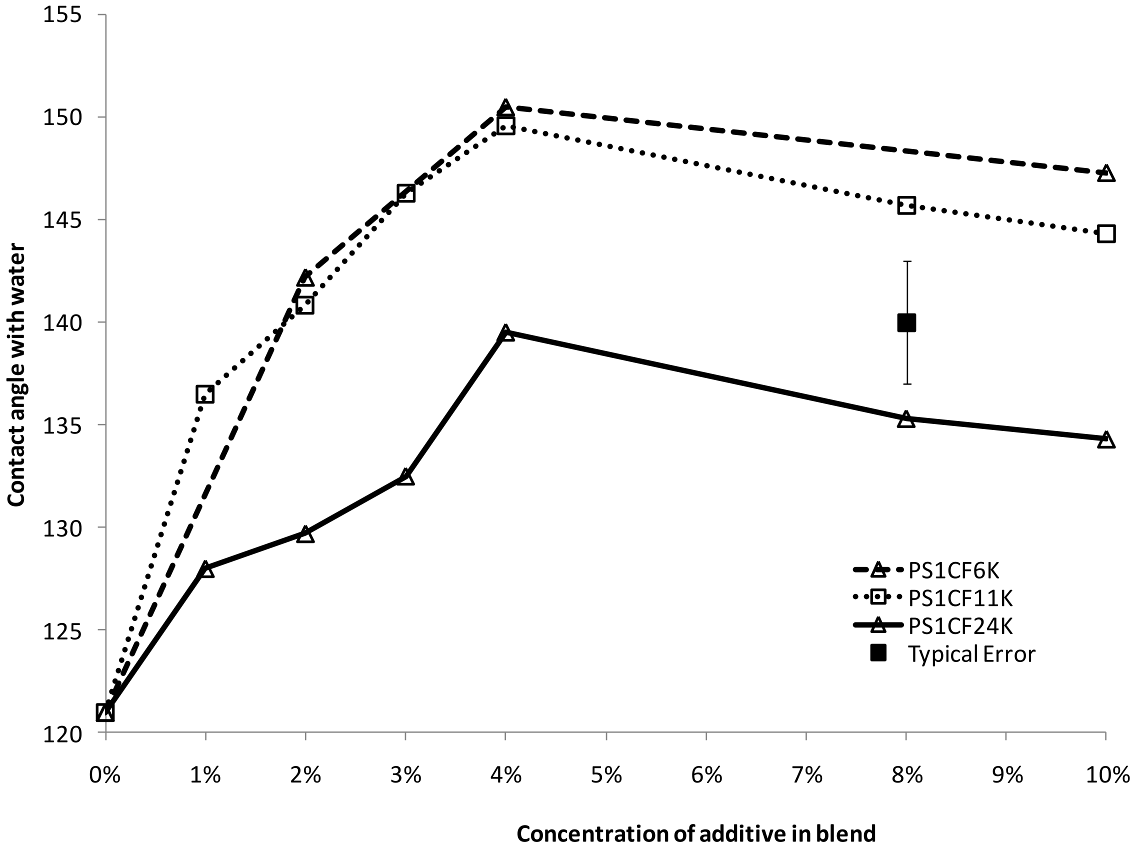


Figure 3. Static contact angles of water on electrospun fibres of PS525 containing end functionalized additive carrying 1CF group of varying molecular weight as a function of concentration of additive.

angle of a little over 120 degrees – substantially higher than that of a thin film of pure polystyrene which has a contact angle of about 90 degrees[17] This dramatic increase of 30 degrees is due entirely to the surface morphology – the mat of fibres being much more heterogeneous/rough than a thin film and the effects of such changes in surface morphology on contact angles is well documented[38,39]. Figure 3 shows the results of contact angle measurements for electrospun fibres of PS525 containing end functionalized additives carrying a single fluoroalkyl end group. Data was collected for fibres containing 1-10 weight % of three different molecular weight additives, PS1CF6K, PS1CF11K and PS1CF24K. It is abundantly clear that the addition of even the smallest quantity of functionalized additive (1% by weight) results in a notable increase is surface hydrophobicity, suggesting that the additives are able to undergo surface segregation during the very short processing time of electrospinning. Moreover, there is a clear relationship between the molecular weight of additive, the concentration of additive and the resulting fibre surface properties. The fibres containing the highest molecular weight additive, PS1CF24K, show a steady increase in contact angle as the concentration increases, rising from 128 degrees at 1% additive to 139 degrees at 4%. It is very interesting to note that at concentrations above 4% the contact angle actually decreases slightly. Fibres containing the lower molecular weight additives, PS1CF11K and PS1CF6K, show similar trends to PS1CF24K, albeit that the trends are shifted to higher contact angles. PS1CF11K and PS1CF6K show similar maximum contact angles of 149 degrees and 151 degrees respectively – the latter just exceeding the threshold contact angle (150 degrees) used to define superhydrophobic surfaces[40]. It is noteworthy that in both cases, concentrations of additive in excess of 4% result in slight reductions in contact angle in a manner consistent with the behaviour of PS1CF24K. The relationship between contact angle and molecular weight is qualitatively similar to that observed in thin films where a reduction in molecular weight also results in an increase in contact angle[17,34]. The relationship between concentration of additive and contact angle is also qualitatively similar to that observed in thin films, at least, for concentrations up to 4%. As discussed previously, the surface properties (contact angles) depend upon the concentration of functionalized additive at the surface of the fibre which in turn is dependent upon the molecular weight of the additive and the concentration of additive[34]. The surface composition of these polymer blends is expected to be different from the composition of the interior or bulk and the distribution of a low surface energy component between bulk and surface, and therefore the surface composition, arises as a result of a series of interrelated phenomena. We have previously discussed[34,41] that there are similarities in the behavior of the fluorinated additives in thin films and that of surfactants in solution, and the formation of a maximum in contact angle at higher concentrations of fluorinated additive may be due in some part to the formation of aggregates of polymer additives in the bulk. It was argued that the fluorinated head groups are not very soluble in the matrix but at low concentrations the additives are molecularly dissolved – just as low

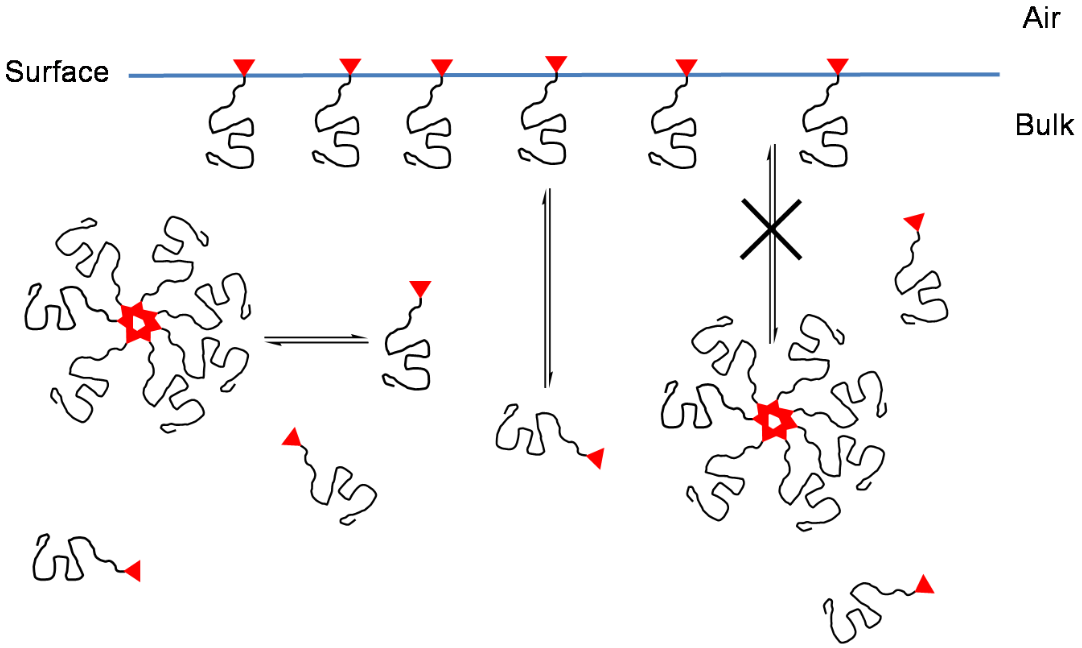


Figure 4. Schematic representation of the equilibria that exist between free and aggregated additive chains in the bulk and how free additive chains are able to surface segregate whilst aggregates do not. Reproduced from ref 34 with kind permission from the Royal Society of Chemistry

concentrations of surfactants are dissolved in water. However, as the concentration of additives increases, there comes a point when the additives start to aggregate – just as surfactants form micelles! In the case of surfactants, the concentration at which this occurs is called the critical micelle concentration (CMC); in the case of fluorinated additives in thin films, aggregation occurs above a critical aggregation concentration (CAC). In the case of micelles, upon reaching CMC, the addition of further surfactant only increases the number of micelles and we have shown that above the CAC in thin films, the addition of further additive merely results in an increase in the number/size of aggregates[41]. The analogy that fluorinated additives behave in a similar fashion to micelles in solution extends to the fact that just as micelles are dynamic, there will be an equilibrium (when above the glass transition of the constituent polymer chains or in the presence of solvent) between free additive chains, molecular dissolved in the bulk phase and aggregates. What is also certain is that the aggregates will diffuse through the bulk at a substantially slower rate than the free chains and in effect only the free chains will be capable of surface segregation, see figure 4. There will also be an equilibrium between free chains at the surface and free chains in the bulk and this equilibrium will be determined by a number of parameters including the molecular weight of the additive, which in turn will dictate the rate of diffusion through the bulk phase, and the packing density of additive chains at the surface. It is certain that these phenomena also occur during the electrospinning process and it is very doubtful that the equilibrium distribution of additives between the bulk and surface of the fibre will be reached in the very short time before the electrospun fibres solidify. Therefore, just as post-spinning annealing of thin films, allows equilibrium distributions to be reached and results in sometimes significant changes in the surface composition/surface properties,[34] so it was found to be the case with electrospun fibres – see later discussion. However, whilst many similarities exist between the behaviour of these additives in the production of spin-cast thin films and electrospun fibres, the data in figure 3 points to some notable differences. In the case of fluorinated additives in thin films, the onset of a maximum in contact angles with additive concentration always resulted in a plateau in contact angles. In the present work we see a maximum in contact angle followed by a consistent decrease in contact angles.

Contact angle measurements were also obtained for fibres electrospun from blends of PS525 and additives carrying 2 and 3 CF groups, PS2CF9K and PS3CF10K – see figure 5. It is clear from this data that for the three additives with very similar molecular weights, increasing the number of CF groups located at the chain end results in an increase the contact angle. This observation is qualitatively consistent with our previous studies on the effect of additive in thin films[17,34]. At all concentrations of additive there is a significant increase in surface hydrophobicity in moving from an additive with 1CF end group to 2CF end groups but little further increase in contact angles for the additive with 3 CF groups. Thus PS1CF11K, PS2CF9K and PS3CF10K have maximum contact angles of 149, 152 and 152.5 degrees respectively. It is worth noting that the increases in contact angle accompanying an increase in the number of CF groups for the same additives in thin films produced by spin-coating (without subsequent annealing) are slightly greater in magnitude. Films containing PS1CF11K,

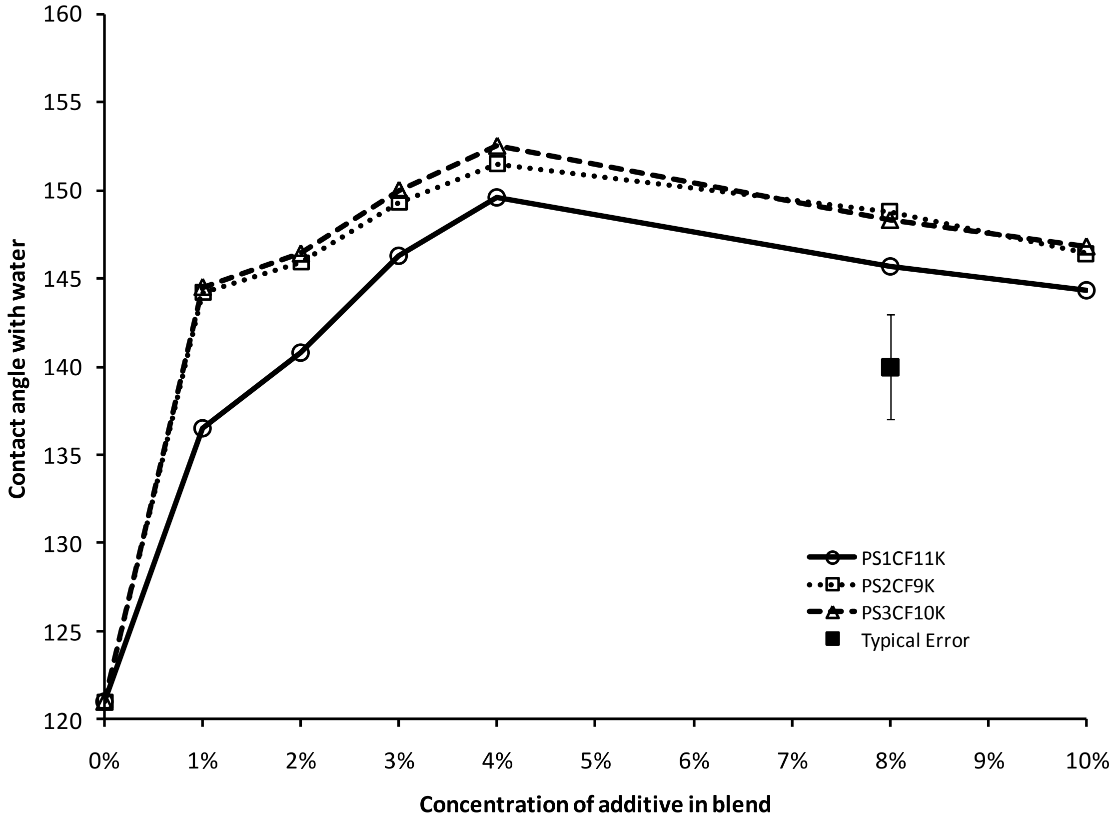


Figure 5. Static contact angles of water on electrospun fibres of PS525 containing end functionalized additives PS1CF11K, PS2CF9K and PS3CF10K as a function of concentration of additive.

PS2CF9K and PS3CF10K at various concentrations show maximum contact angles at 95.5, 100.4 and 102.7 degrees respectively[34]. Furthermore, in a manner consistent with the data in figure 3, each set of data in figure 5 show a maximum at 4% additive, followed by a reduction of up to 6 degrees in contact angle as the concentration increases to 10%. Based on all of our previous studies this reduction in contact angle at higher concentrations is counterintuitive and although it could be argued that the decrease is within the error limits, the consistency of this observation for five separate sets of data shows that this effect is a real effect. It is well understood that contact angles are highly dependent upon both surface chemistry (surface energy) and surface roughness and whilst thin spin cast films are generally speaking rather smooth with a root mean square roughness in the order of 1 nm or less, the surface of the fibre mats generated by electrospinning are inherently rough and heterogeneous. In order to gain some understanding of the surface elemental composition of the electrospun fibres, x-ray photoelectron

Table 2. XPS analysis data for electrospun fibres of PS525 containing 4% and 10% of PS3CF10K

Sample	**Atomic % from peak areas**			**Ratio F:C**
	Fluorine	**Carbon**	**Oxygen**	
PS3CF10K – 4%	10.9	88.4	0.8	0.123
PS3CF10K – 10%	18.3	80.9	0.9	0.226

spectroscopy (XPS) analysis was carried out on fibres containing 4% and 10% PS3CF10K. XPS analysis measures the near surface elemental composition of samples to a depth of approximately 10 nm. These particular samples were chosen as they should help relate any changes in surface composition to the unexpected decrease in contact angle. The XPS data in table 2 (and the full XPS spectra for these two samples which are included as electronic supporting information) shows that there is a significantly higher fluorine content near the surface of the fibres spun with 10% PS3CF10K and the fluorine : carbon ratio increases from 0.123 to 0.226 as the concentration of PS3CF10K increases from 4% to 10%. This of course is not unexpected and suggests that the decrease in contact angles observed at higher concentration of additives (figs 3 and 5) cannot be explained in terms of surface elemental composition and surface energy. This would suggest that the reduction in contact angle is more to do with the surface morphology/surface roughness. An investigation of the ESEM images of the fibres obtained with different concentrations of additive reveal no significant differences either in fibre size, shape or morphology. In all cases, uniform ribbon-like fibres were obtained – similar in nature to those illustrated in figure S1C – with no suggestion of beading. In addition, measurements of average fibre diameter did not show any significant relationship between fibre diameter and concentration of additive and at this point investigations to solve this unexpected relationship between concentration of additive and contact angle are ongoing.

Annealing of electrospun fibres

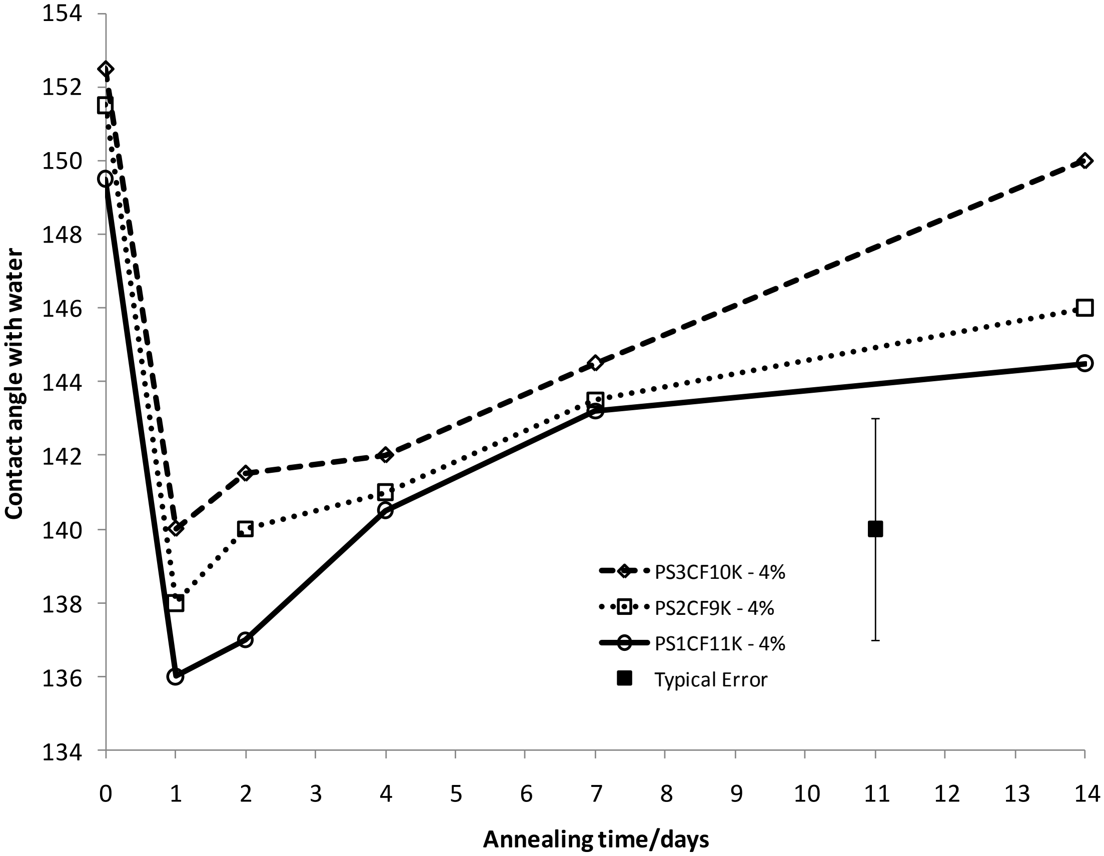


Figure 6. The effect of annealing time on static contact angles of water on electrospun fibres of PS525 containing 4% of PS1CF11K, PS2CF9K and PS3CF10K.

It has been reported previously[17,34] (and alluded to above) that annealing above the glass transition temperature (T_g) can lead to enhanced surface segregation. In the present study, selected fibre mats of PS525 containing 2%, 4% and 10% of PS1CF11K, PS2CF9K and PS3CF10K were annealed to assess the impact on surface properties. However, since annealing the mats of electrospun fibres at temperatures well in excess of T_g for prolonged periods of time would effectively destroy the fibre structure and result in a film, annealing of the fibres was carried out at a temperature of 100^o C - the temperature corresponding to the onset of the glass transition temperature of the fibres (as determined by DSC). At this temperature the matrix polymer (PS525) will experience a small but sufficient increase in free volume and thermal energy to allow the much lower molecular weight fluorinated additives to diffuse through the bulk without destroying the structure of the fibres. It was also expected that at this temperature the rate of diffusion and therefore surface segregation would not be a rapid process. The fibres were annealed at 100^{o} C for up to 2 weeks, samples being withdrawn for analysis at intermediate times. Fibres of pure unmodified PS525 were also annealed under the same conditions and time periods as a control. Figure 6 shows the results of annealing fibres contain 4% of each of the three additives. The most startling observation of the data in figure 6 is the significant drop in contact angles after annealing for 24 hours. The unmodified pure PS525 also showed a drop in contact angle – from 121 degrees to 114 degrees with prolonged annealing. These precipitous falls in contact angle upon annealing can be easily rationalized. It was observed that after the initial electrospinning of the fibres, the resulting mats had a certain depth to them; the fibre mats were 3 dimensional! In contrast, after annealing at 100^{o} C for 24 hours it could be seen that the mats had lost some of that 3 dimensional structure – it was as if they had been gently compressed or flattened. In reality, it would appear as if at the onset of the glass transition temperature, the fibres have softened enough to become compressed by gravity. Although the structure of the individual fibres remained largely unchanged, after prolonged annealing some overlapping fibres appear to have 'melted' into each other. This is evident in the ESEM image of a mat of PS525 containing 2% PS3CF10K after two weeks – figure 7. We believe that this softening and induced loss of depth probably results in a reduction in surface roughness and a concomitant reduction in the contact angle. Interestingly, although the unmodified fibre continues to show a steady reduction in contact angle for the duration of the annealing process, each of the samples containing fluorinated additive show a minimum in contact angle after 24 hours followed by a sharp recovery in contact angle. Furthermore, although at first glance the behaviour of fibres modified with each of the end functionalized additives (figure 6) would appear to be qualitatively similar, on closer inspection it is clear that significant and consistent differences exist. After 2 weeks, the contact angles for fibres containing 4% PS1CF11K are beginning to plateau, suggesting that the distribution of additive between surface and bulk is close to equilibrium and the contact angles with water after this period has reached 144.5 degrees. In the case of PS2CF9K the rate of increase in contact angle is decreasing, implying that the distribution of additives is approaching equilibrium and the contact angles for fibres containing 4%

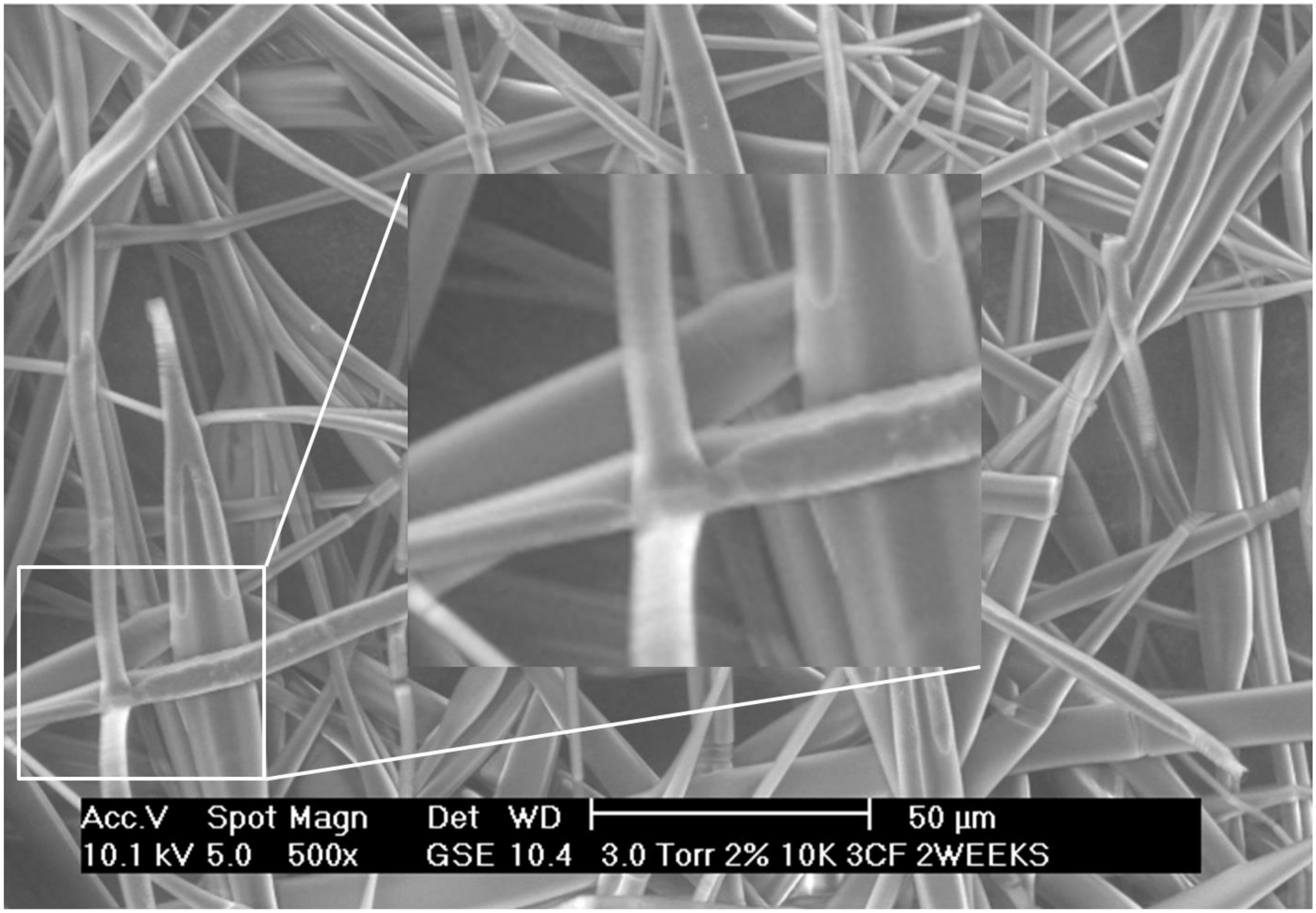


Figure 7. ESEM image of a mat of PS525 containing 2% PS3CF10K after two weeks annealing at 100^{o} Celsius. Inset image shows how two overlapping fibres appear to have fused into each other during annealing.

PS2CF9K after 14 days is slightly higher than PS1CF11K (and still rising) at 146 degrees. In the final case, PS3CF10K, the slope of the line is fairly steep and constant between day 4 of annealing and 2 weeks and the rate of increase in contact angle shows no sign of abating, suggesting the system is still some way from reaching equilibrium. Even so, after annealing for 14 days the contact angles of fibres containing 4% PS3CF10K is notably higher (and rising) than fibres containing PS1CF11K and PS2CF9K at 150 degrees. Can this behaviour be rationalized?

That fibres containing 4% of PS3CF10K show the highest contact angles is entirely consistent with all our previous data. However, the behaviour described above would suggest that fibres containing 4%

PS3CF10K require longer annealing times to reach equilibrium than fibres containing 4% PS2CF9K which in turn require longer annealing times than fibres containing 4% PS1CF11K. The most plausible explanation relates to the relative extent of aggregation in the bulk of the various additives. We have already proposed a model to describe the behaviour of the end functionalized polymer additives and the equilibria that exist between i) free additive chains and aggregates in the bulk and ii) free additive chains in the bulk and at the surface – see figure 4. Such a model suggests that only free additive chains in the bulk are likely to be able to diffuse to the surface and moreover, the concentration of free additive chains in the bulk will depend on the position of the equilibrium between free chains and aggregates. In turn the position of this equilibrium is certain to be effected by the nature of the aggregation. We have previously reported[41] studies which have shown that the extent to which these additives aggregate varies greatly depending upon the number of CF end groups and the concentration of additives. Small angle neutron scattering data has shown that thin films containing analogous additives with 2CF groups form star like aggregates comprising of 6-7 individual additive molecules above a critical concentration of additive whereas additives with 4CF groups formed aggregates which resemble discrete multi-lamellar vesicles with dimensions in the order of 100-200 nm. It is possible that in the current study, additives with nearly identical molecular weights and increasing numbers of CF groups will become progressively less compatible with the bulk/matrix polymer and similarly prone to an increasingly strong tendency to aggregate which in turn will inhibit the rate of surface segregation. Given the magnitude of the error bars and the relatively small differences in behaviour, this hypothesis must be further examined before firm conclusions can be drawn.

XPS data for fibres containing 4% PS3CF10K before and after annealing further supports the above discussion. The fluorine : carbon ratio for the fibres before annealing was 0.123; after annealing for 24 hours this ratio was essentially unchanged at 0.122 confirming that the initial drop in contact angle was due to changes in surface roughness. However the F:C ratio increased to 0.157 for the fibres annealed for 14 days confirming that the increased contact angle after prolonged annealing can be attributed to an increase in the concentration of fluorine at the surface, arising from enhanced surface adsorption of the fluorinated additives.

Contact Angle Measurements of Fibres spun from DMF/THF (3:1 v/v)

Preliminary electrospinning experiments using a blend of DMF/THF (3:1 v/v) as the spinning solvent resulted in fibres which were cylindrical (rather than ribbon like), much more uniform and much smaller in fibre diameter than when using THF as the spinning solvent – see figure 2. This reduced fibre diameter had a significant impact on the surface properties of fibres produced from polystyrene containing the fluorinated additive. Blends of PS235 containing 2%, 4% and 10% of PS3CF10K were prepared and the resulting fibres showed substantially higher contact angles than previously obtained, although it should be noted that unmodified PS fibres also showed much higher contact angles (greater than 140 degrees) than analogous unmodified fibres spun from THF. This would suggest that the increased hydrophobicity when using the mixed solvent is in part due to the size and shape of the fibre. Qualitatively, the relationship between additive concentration and contact angle was the same as previously described for fibres produced using THF; namely that a maximum contact angle was observed for fibres containing 4% additive and higher concentrations of additive resulted in a slight decrease in hydrophobicity. The highest contact angle obtained for fibres spun from the mixed solvent, containing 4% PS3CF10K was 158 degrees, a value of notable importance as it is a higher contact angle that that obtained by Lim et al[42] (153 degrees) for electrospun fibres of a pure fluorinated polymer (poly(2,2,2-trifluoroethyl methacrylate). Moreover, a contact angle of 158 degrees is the same value of contact angle obtained by Steckl et al[14] for co-axially spun fibres of poly(ε-caprolactone) with a sheath of Teflon AF – an amorphous fluoropolymer. Conceptually and in reality the in situ surface migration of a fluorinated polymer additive is an attractive alternative to co-axial electrospinning to produce superhydrophobic fibres resulting in fibres with similar surface properties prepared in a one step process. Moreover, the inherent compatibility of the additives described in the current work may result in superior durability of surface properties and no concerns over the adhesion between the core and sheath layers in co-axial spun fibres. Further investigations into the use of DMF/THF as a solvent for electrospinning surface functionalized superhydrophobic fibres are ongoing and will be reported in the near future.

Conclusions

We report here a facile methodology for the production of superhydrophobic fibres by electrospinning polystyrene containing fluoroalkyl end capped polymer additives. Spontaneous surface segregation of the additives during the spinning process results in fibres with fluorine-rich surfaces and superhydrophobic properties. The use of THF as a spinning solvent resulted in ribbon like fibres with a distribution of diameters measured in the 10s of microns. Additives with 1, 2 and $3C_8F_{17}$ groups were investigated and increasing the number of fluoroalkyl groups lead to an increase in surface hydrophobicity. However, in contrast to previous work carried out in our group on spin-cast films, a maximum contact angle was observed (at 4% in all cases) followed by a slight reduction in contact angle. XPS data showed that fibres containing 10% additive had a higher near-surface fluorine concentration suggesting that the reduction in contact angles at higher concentration of additive may be due to a surface roughness effect although this is not yet confirmed. Annealing of the THF spun fibres at 100^o C (the onset of T_g) resulted in an initial drop in contact angle followed by a subsequent recovery in hydrophobicity. This behaviour was attributed to an initial change in morphology (reduction in surface roughness) followed by enhanced surface adsorption of the additive.

Some preliminary results of the use of a mixed solvent of DMF/THF (3:1 v/v) as the electrospinning solvent are reported. The use of this mixed solvent resulted in fibres with a much more uniform structure and smaller size. The resulting fibres, with average diameters in the region of 1-2 microns had significantly enhanced hydrophobicity. Fibres produced from PS235 containing 4% PS3CF10K were superhydrophobic with a static water contact angle of 158 degrees.

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Table of Contents use only

Manuscript title “Electrospinning Superhydrophobic Fibres Using Surface Segregating End-Functionalized Polymer Additives”

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