DEVELOPMENT OF MAGNETIC FABRICS WITH TUNABLE HYDROPHOBICITY

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DEVELOPMENT OF MAGNETIC FABRICS WITH TUNABLE HYDROPHOBICITY

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at Virginia Commonwealth University.

by

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Virginia Commonwealth University
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Abstract

DEVELOPMENT OF MAGNETIC FABRICS WITH TUNABLE HYDROPHOBICITY

By Thu Ho, M.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at Virginia Commonwealth University.

Virginia Commonwealth University, 2012

Major Director: Dr. Gary Tepper
Professor and Chair, Department of Mechanical and Nuclear Engineering

Polystyrene (PS) fiber mats incorporating iron (Fe) particles were fabricated by electrospinning and the hydrophobicity of the resulting magnetic fabrics was investigated with and without an applied magnetic field. The results show that the hydrophobicity (as measured using water droplet contact angle) increases in the presence of a magnetic field and the hysteresis in the advancing/receding contact angle (a measure of the stickiness of the surface) decreases in the presence of a magnetic field. It is also shown that the contact angle and hysterises increase with decreasing fiber diameter and mat thickness.
1.1 Introduction:

Superhydrophobic surfaces are characterized by a water droplet contact angle (WCA) larger than 150 degrees and are being investigated for numerous applications including self-cleaning surfaces and drag reduction. Superhydrophobicity is the result of a combination of hydrophobicity (low surface free energy) and micro or nano-scale surface roughness. Synthetic superhydrophobic surfaces have been produced using many techniques including layer-by-layer deposition, chemical deposition, sol-gel processing and solution casting, laser/plaster/chemical etching, lithography and electrospinning. In recent years, electrospinning has attracted significant attention for its ability to produce polymer or polymer composite fibrous mats with high specific surface area and micro or nano-scale surface roughness. In this paper electrospinning was used to produce hydrophobic and superhydrophobic polystyrene and polystyrene/iron composite fibrous mats with different average fiber diameter and mat thickness. Contact angle measurements were performed to determine the effect of surface morphology and magnetic environment on hydrophobicity. The results show that the hydrophobicity of the surface increases with decreasing fiber diameter. For polystyrene/iron composite fabrics, the hydrophobicity can be further increased through the application of an externally applied magnetic field. At this time, the exact mechanism through which the magnetic field increases the surface
hydrophobicity is uncertain, but is likely due to either a field induced change in surface morphology (roughness) or a field induced change in surface chemistry (free energy). The purpose of this initial paper is to present our preliminary qualitative findings on the hydrophobicity of magnetic fabrics. The ability to adjust the hydrophobicity of a surface using an externally applied magnetic field could have many applications in areas such as liquid sampling, microfluidics, flow control and surface chemistry.
1.2 A Review of Theories on Superhydrophobic Materials

The wettability of a surface can be characterized by the static contact angle between a water droplet and the surface. If the contact angle is less than 90°, the surface is deemed hydrophilic whereas if the contact angle is greater than 90°, the surface is hydrophobic. If the contact angle is between 150° and 180°, the surface is superhydrophobic. A droplet may form either a homogeneous interface on a solid surface, or a composite interface on a rough surface where air pockets trapped between the surface and the droplet form a non-wetting phase and can lead to the very large contact angles characteristic of superhydrophobicity. The surfaces prepared and characterized in this paper are of the latter case. The Wenzel equation developed for a homogeneous solid-liquid interface was extended by Cassie and Baxter for the composite interface. The contact angle for the composite surface can be calculated with the following equation

$$\cos \theta = R_f f_{SL} \cos \theta_o - f_{LA}$$

where $\theta$ is the contact angle of the rough surface, $\theta_o$ is the contact angle of the smooth surface, $R_f$ is the roughness factor, defined as the ratio of the solid-liquid area to its projection on a flat lane, $f_{SL}$ and $f_{LA}$ are fractional geometrical areas of the solid-liquid and liquid-air interfaces under the droplet, respectively. From this equation, it can be seen that the contact angle on the rough surface depends on both geometric factors as well as the contact angle of the smooth surface (a measure of the surface free energy).

Contact angle hysteresis, the difference between the advancing and receding contact angles of a droplet moving along a surface, can be used to characterize the “stickiness” of a hydrophobic surface. A low contact angle hysteresis suggests a very
low water roll-off angle (the angle at which the droplet will roll off the surface) and this property is very important in some applications such as self-cleaning surfaces and drag reduction. A high contact angle hysteresis results in a high roll-off angle and in extreme cases can result in the so-called gecko state where a water droplet sticks to the surface and the surface can be inverted with the water droplet suspended beneath. That is, while somewhat counterintuitive, a surface can be both sticky and superhydrophobic. A water droplet placed onto a sticky superhydrophobic surface will have a very high contact angle but will also adhere to the surface. Our results have shown that an externally applied magnetic field can affect the contact angle hysteresis (stickiness) of a magnetic fabric. For the surfaces studied in this work, the applied magnetic field was found to decrease the contact angle hysteresis (stickiness). Therefore, it may be possible, for example, to collect water droplets on a sticky superhydrophobic surface and release them using a magnetic field.

Figure 1: Contact Angle Hysteresis
1.2.1 History of Superhydrophobic Materials

Research on the phenomenon of high contact angles - superhydrophobic surfaces started in 1907 when Ollivier observed that contact angles of nearly 180° on surfaces coated with arsenic trioxide, soot and lycopodium powder. In 1923, Coghill and Anderson created surface with high contact angle of about 160° by depositing stearic acids on the rough surface of galena. Research on superhydrophobic surfaces continued to received, however limited, attention before the mid-1990s, which was focused on the relation between contact angles and surface geometry, observations of superhydrophobic phenomena of triticum plant leaves, surfaces of ducks’ feathers, and insect cuticles. In 1997, Neinhuis and Barthlott explained the origin and the universal principle of the “lotus effect” in nature, therefore reactivated research on this topic. It was revealed that the epicuticular wax crystalloids of the plant surface are responsible for their self-cleaning properties. Since then, a lot of research have been distributed to understanding the surface structures of different plants and animals, and then to fabricate similar structures artificially. Additionally, there have also been tremendous effort in is improving the performance of chemical materials through surface modification. Beyond the research on fabrication superhydrophobic surfaces, recently, research on potential functional applications of superhydrophobic coatings has also been gaining a lot of attentions.
1.2.2 Characterization of Superhydrophobic Material

Many methods have been developed to characterize the superhydrophobicity of the surface, such as contact angle, tilt angle and multiresonance thickness-shear mode sensors (MTSM). Contact angle measurement is always the main method for the characterization of superhydrophobic surfaces. The superhydrophobic states can be further classified considering the contact angle hysteresis.

a. Static Contact Angles of Water

The static contact angle measurement of water is often used to characterize the superhydrophobicity. However, many reports show that various values of the contact angle from around 150 to larger than 179 can be observed for similarly shaped water droplets of 4 mL or 5 mL.\(^{33-37}\) This phenomenon is caused by the different fitting modes of the static contact angle, which are ellipse fitting, circle fitting, tangent searching, Laplace–Young fitting and so on. For the same water droplet of 5 mL, under ellipse fitting, circle fitting and tangent searching modes, the contact angle is around 156; however, for Laplace–Young fitting, the contact angle is larger than 179. This error is related to the deformation of the water droplet caused by gravity. Therefore, the difference of contact angles from 150 to 179 does not reflect the real situation of surface wetting, if the fitting mode is not clearly mentioned. It should be noted that the contact angle is influenced by the volume of the water droplet and the gravity force. To reduce the influence of the deformation of the water droplet caused by gravity force, it was proposed that a much smaller water droplet should be employed when measuring water contact angle. However, because of the low surface adherence of many superhydrophobic surfaces,\(^{38}\) it is very hard to obtain a water droplet
with a volume lower than 4 mL. The contact angle must be measured with the same volume of water droplet, when comparing the superhydrophobicity for different surfaces.

b. Contact Angle Hysteresis

Conventionally, superhydrophobicity means not only a high contact angle, but also a low hysteresis of the contact angle. The low hysteresis of the contact angle of the superhydrophobic surface is responsible for the self-cleaning properties, which means that a water droplet can easily roll off the surface and remove dust from the surface. Self-cleaning is one of the most important origination of the application and function of superhydrophobic surfaces. Therefore, many of methods and techniques have been developed to measure the contact angle hysteresis, including the tilt angle, the advancing/receding angle, contact angle measurements with surfactant solution, MTSM, and so on.

c. Tilt Angle

The tilt angle refers to the critical angle between the substrate and the horizontal, below which the water droplet begins to move upon elevating one end of the substrate. When the tilt angle of a superhydrophobic surface is lower than 10, it means that this surface is a self-cleaning surface. It should be pointed out, however, that the tilt angle does not equal, but reflects, the difference between advancing and receding contact angles. The combination of micro- and nano-roughness is helpful for obtaining surfaces with high contact angle and low tilt angle.39
1.2.3 Fabrication of Superhydrophobic Material

As pointed out above, generatesuperhydrophobic surfaces can be fabricated with two main approaches: increasing directly the surface roughness of low-surface-energy materials; or fabricating a suitable surface roughness with certain materials and then to modify the as-prepared surface with low-surface-energy materials.

Rough surfaces can be fabricated by chemical and physical methods. A few methods used to fabricate rough surfaces are wax solidification, lithography, vapor deposition, template method, polymer reconformation, sublimation, electrohydrodynamics/electrospinning, plasma technique, sol-gel processing, electrochemical method, bottom-up approach for the fabrication of nano-arrays, hydrothermal synthesis, layer-by-layer methods, and one-pot reaction.

Till now, there are various low-surface-energy coatings developed to modify organic and inorganic rough surfaces to fabricate superhydrophobic surfaces. A few methods of low-surface-energy coatings are self-assembled monolayer of alkanethiols, organic silanes, and fatty acids, surface modification with aromatic azide, and spin-coating perfluorononane.

The method employed here in this research is electrospinning, which will be explained in more details in the next section.
1.3 Electrospinning

Electrospinning is a process that employs electrostatic forces to draw polymer fibers from a solution. The main components of the electrospinning process are shown in Figure 1 and consist of a syringe feeder system containing the polymer solution, a collector system where the fiber will be deposited and a high voltage power supply to provide the electrical force. The liquid in the syringe is charged (either positively or negatively) with respect to the grounded collecting electrode and the liquid surface distorts into a conical shape known as a Taylor cone, due to a competition between the applied electric force and the liquid surface tension. When the electric field reaches a critical value, the surface tension of the solution is overcome by the electric force and a charged liquid jet emerges from the tip of the Taylor cone. Polymer fibers are formed in the jet when the polymer concentration is high enough for chain entanglement to occur and the fibers dry as the solvent evaporates and are deposited on the grounded target. However, because the fibers are electrically charged, surface deposition can be impeded by surface charge accumulation, particularly on surfaces with very low electrical conductivity. Deposition can even be impeded on conducting substrates if the deposited polymer layer becomes sufficiently thick to electrically insulate the surface, thereby preventing charge dissipation. In this case, the positively charged substrate repels the positively charged fibers and prevents deposition. Previously we showed that a negative ion source, used in conjunction with a positively charged electrospinning source, can be used to neutralize surface charges in situ and facilitate uniform fiber deposition\textsuperscript{19}. The fiber diameter in an electrospinning process can be adjusted by changing processing parameters such as solute concentration,
solution conductivity, electrostatic force and liquid surface tension. For the polystyrene solutions used in this study, the polystyrene fiber diameters were adjusted by changing the solute concentration while keeping all other parameters constant.

1.4 Magnetic Nanofiber

One-dimensional magnetic nanostructures have been recently gaining attention for their distinctive properties that are not shown in their bulk or particle form\textsuperscript{27-29}. These nanostructures offer a wide range of applications such as ultrahigh-density data storages, sensors, a drug delivery system, and bullet proof vest\textsuperscript{30-32}. The key factor in fabricating such composite nanostructures are the achievement of uniform dispersions of magnetic particles and the choice of appropriate methods. Below approximately 100 nm in diameters, ferromagnetic particles such as Iron Oxide no longer exhibit the cooperative phenomenon of ferromagnetism found in the bulk particles, due to thermal fluctuations sufficient to reorient the magnetization direction of entire particles. Instead, such nanoparticles are superparamagnetics, exhibiting strong paramagnetic properties with large susceptibility. In a uniform external magnetic field, such superparamagnetic nanoparticles within the fibers would be expected to align with their magnetic moments in the direction of the magnetic field such that when the fiber is deformed, extra energy is needed to disrupt this alignment of the nanoparticles within the fiber, resulting in its increased stiffness. In a nonuniform magnetic field, the magnetic nanofibers should also deform and bend in the direction of the gradient of the magnetic field. These changes in stiffness and shape should be completely reversible, since the particle magnetic moment and fiber
orientations should relax to their original distributions on removal of stress and magnetic field. The relative magnitudes of the stiffness enhancement and fiber deformation are expected to increase as the diameter of the embedding polymer fiber is reduced.
{CHAPTER 2 EXPERIMENTAL SETUP}

This chapter provides information about the various parameters and apparatus used for the study. This includes detailed descriptions on preparation of polymer solutions, fabrication of fiber mats by electrospinning, and the characterizations of samples by water contact angle measurements, Thermal Gravimetric Analysis (TGA) and scanning electron microscopy (SEM).

2.1 Material

Polystyrene (PS), Toluene and Dimethylformamide (DMF) were purchased from Sigma-Aldrich Co. LLC., and used as received without further purification. Iron nanoparticles were purchased from READE Advanced Materials.

2.2 Preparation of Polymer Solutions

PS solutions were prepared at four different concentrations ranging from 10% to 25% by weight. The solvent composition was kept constant at 70% Toluene and 30% DMF. PS concentrations, however, were varied to achieve various fiber diameters. PS as purchased came as solid beads. Therefore, after being added to the solvents at a designated weight percent, the solution was left to dissolve for an extended amount of time (typically 24 hours) to ensure homogeneous solutions.

In order to make electrospun PS mats with embedded magnetic particles, iron nanoparticles (60-80 nm) were added to the prepared PS solutions above at the same weight percent as the PS beads. Therefore, after solvent evaporation, the resulting dry mat
consists of half PS and half Iron particles by weight. Iron nanoparticles as purchased are pyrophoric, which means they can ignite spontaneously in air. Therefore the process of adding these particles to the PS solutions was performed inside of a glove box filled with inert gas (Argon). The nanoparticles also tend to agglomerate. Therefore, after the solutions were prepared; they were sonicated for several hours before electrospinning. Branson 2510 Ultrasonic Cleaner was used as an ultrasonic bath for this purpose. The magnetic PS solutions were electrospun shortly after the sonication.

2.3 Electrospinning

The electrospinning apparatus consisted of a high voltage D.C. source, an infusion pump, a corona (negative ion source for neutralizing surface charge) and a rotating aluminum cylindrical drum. Substrate samples were mounted using two small pieces of copper tape (typically 2 x 4 mm) onto a grounded aluminum drum acting as a collector. This hexagonal cylindrical drum is 6.5 inches long, the spacing between parallel faces is 1 inch and each face width is 0.55 inches. The drum was mounted to a lathe (Micro lathe II, Model 4500), and was rotated at 1200 rpm via belt connection to an AC motor (Marathon Electric, Cat No. S102). An electrospinning needle assembly and a corona assembly were positioned on the opposite sides of the drum axis. The electrospinning needle assembly consisted of a flat tip stainless steel (SS) 23G needle (Becton-Dickinson, PrecisionGlideTM) of length ½”. It was connected to a 1 cc plastic syringe (National Scientific Company, #S7510-1) containing the designated polymer solution. This solution syringe was placed in an infusion pump (Harvard Apparatus PHD2000). The flow rate was set to 0.8 µL/min.
The distance between the needle tip and the drum axis was 7 cm. A voltage of 7.5 kV was applied to the needle by a Matsusada Precision Inc. power supply (Model AMT-10810-LCS). The corona was placed 4.5 mm from drum surface, its tip coaxial to the needle tip. A negative voltage of 3.5 kV was given to the corona with Spellman power supply (model CZE1000R). The collector drum was electrically grounded. It was also ensured that all other electrical devices were properly grounded at one end. All voltage and current measurements were taken either directly from the power supplies or using an Agilent 34401A digital multimeter and/or a Fluke 80k-40 HV probe. Temperature and humidity measurements were taken before each experiment using a Vaisala HM 34 meter.

FIGURE 2: Schematically Outlines the Electrospinning Apparatus Setup.
2.4 Superhydrophobicity and Hysteresis Measurement

The water contact angle and hysteresis (difference in advancing and receding contact angles) were measured with a Game-hart Model 500 Advanced Goniometer. For the measurement of contact angles, droplet size was kept constant at a volume of about 5 \( \mu l \) (2.1 mm droplet diameter).

Two different types of permanent magnets were used to test the effect of a magnetic field on the hydrophobicity of the magnetic-particle-embedded mats.

2.5 Thermal Gravimetric Analysis (TGA)

Because the vast majority of the magnetic particles were embedded within the PS fibers, scanning electron microscopy (SEM) could not be used to visualize the particles. Therefore, TGA was used to ensure that the fiber mats contain the same weight composition of PS and Iron nanoparticles (1:1) after electrospinning. Pre-weighed samples were heated in the TGA furnace to remove the PS and then weighed again to determine the weight of the remaining Iron particles.

2.6 Scanning Electron Microscopy (SEM)

The morphology of the fiber mats was characterized using Hitachi Scanning Electron Microscope. The parameters for microscopy included beam voltage of 3-5 kV, working distance of 6 mm, detector bias of +400 V and column aperture of 30 mm. The samples were mounted to stainless steel sample holders of 0.5 inch diameter using carbon adhesive tape. Since the samples were non-conductive, they were coated with carbon paint to add conductivity. Samples were then sputter coated in platinum for 20 minutes. Due to the extra conductivity of carbon paint, comparatively clearer imaging was obtained.
3.1 Effect of Fiber Diameter

Electrospun PS mats were deposited onto glass substrates from 10%, 15%, 20% and 25% PS solutions by weight for 10 minutes, 6.7 minutes, 5 minutes and 4 minutes, respectively. The deposition times were calculated to ensure the same fiber mass deposited on the substrate for all samples. Figure 3.a-d show SEM images of the resulting samples and Table 1 gives the average fiber diameter for each PS concentration.

**TABLE 1: Fiber Diameter for electrospun mats of different PS concentration**

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<tr>
<th>Diameter (µm)</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
<th>25%</th>
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<tr>
<td></td>
<td>0.3</td>
<td>0.5</td>
<td>0.8</td>
<td>0.9</td>
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From the images in figure 3 it can be seen that, in addition to a decrease in fiber diameter with decreasing PS concentration, there is also a change in morphology. At PS concentrations below 20% large beads begin to form along the length of the fibers. The beads are evident in figure 3b (15% solution) and become profuse in figure 3a (10% solution). The so called “bead-on-string” morphology is very common in electrospinning\textsuperscript{21-23}. The presence of the beads in the lower concentration samples makes it difficult to directly correlate the measured hydrophobicity with changes in fiber diameter alone since another morphological change (the formation of beads) is also occurring. The average fiber diameters reported here were obtained from the fiber regions of the mats (between the beads).
Figure 3.a: SEM image of fibers electrospun from 10% PS solution

Figure 3.b: SEM image of fibers electrospun from 15% PS solution
Figure 3.c: SEM image of fibers electrospun from 20% PS solution

Figure 3.d: SEM image of fibers electrospun from 25% PS solution

Figures 4 and 5 show the water contact angle and hysteresis measurements of each of the samples. The data of figure 4 shows that the contact angle decreases significantly (by approximately 16 degrees) as the average fiber diameter increases by 200 nm. The data of figure 5 shows that the contact angle hysteresis decreases by nearly 40 degrees as the average fiber diameter increases by 200 nm.
The water droplet contact angle is a measure of the wettability of a surface and if the contact angle is less than 90°, the surface is deemed hydrophilic whereas if the contact angle is greater than 90°, the surface is hydrophobic. If the contact angle is between 150° and 180°, the
surface is superhydrophobic. A droplet may form either a homogeneous interface on a solid surface, or a composite interface on a rough surface where air pockets trapped between the surface and the droplet form a non-wetting phase and this composite interface is what leads to the very large contact angles characteristic of superhydrophobicity. The fiber-based surfaces prepared and characterized in this paper result in a composite interface where the fibers form the wetting phase and the spaces between the fibers are filled with air and form the non-wetting phase. The Wenzel equation developed for a homogeneous solid-liquid interface was extended by Cassie and Baxter for the composite interface \(^{13-15}\). The contact angle for the composite surface can be calculated with equation (1). The increase in contact angle with decreasing average fiber diameter indicates that the surface roughness factor (the fractional percentage of the water droplet contacting the wetting phase (polymer) versus the non-wetting phase (air)) is higher for the mats with fine fibers and large diameter beads. The contribution of the beads to the roughness factor is expected to be significant based on the images of figure 1, but has not been quantified in the present study.

Contact angle hysteresis, the difference between the advancing and receding contact angles of a droplet moving along a surface, can be used to characterize the “stickiness” of a hydrophobic surface \(^{16}\). A low contact angle hysteresis suggests a very low water roll-off angle (the angle at which the droplet will roll off the surface) and this property is very important in some applications such as self-cleaning surfaces and drag reduction. A high contact angle hysteresis results in a high roll-off angle and in extreme cases can result in the so-called gecko state where a water droplet sticks to the surface and the surface can be inverted with the water droplet suspended beneath\(^{20}\). That is, while somewhat counterintuitive, a surface can be both
sticky and superhydrophobic. A water droplet placed onto a sticky superhydrophobic surface will have a very high contact angle but will also adhere to the surface.

The data of figure 4 shows that the contact angle hysteresis increases significantly with decreasing average fiber diameter. This means that the surface is becoming stickier (transition to gecko state) as the average fiber diameter decreases but this result is more difficult to explain in terms of the observed fabric morphologies. One possibility is that, because of capillarity, the gecko state is favored by the presence of a multitude of small air pockets rather than a few large air pockets.

3.2 Effect of Mat Thickness

Fiber mats of increasing weight/thickness were deposited from 25% PS solutions on a glass substrate to investigate the effect of the mat thickness on hydrophobicity and hysteresis. The coating weight/thickness was varied by increasing the deposition time from 2 minutes to 5 minutes with all other processing parameters remaining constant. Figures 6 and 7 show the water contact angle and hysteresis measurements of the 25% PS samples as a function of deposition time. The results show that increasing the mat thickness initially decreases both the water contact angle as well as the contact angle hysteresis and then levels off. We believe that this indicates that the fiber density (number of fibers per unit surface area) initially increases during the time below 4 minutes when the first complete fiber layer is being formed. After the creation of the first complete layer, the fiber density remains essentially constant and the observed changes in contact angle and hysteresis with deposition time are small. The incomplete fiber layer will exhibit a higher roughness factor since the ratio of the wetting phase to the non-wetting phase is small (few fibers) and will, therefore, have a higher contact angle than the thicker layers.
The incomplete fiber layer will also exhibit higher capillary forces (larger hysteresis) because the air pockets formed between the fibers terminate on the glass substrate and form a closed air pocket. In thicker fiber mats containing multiple layers the air pockets are open and connected through pathways between layers and, therefore, the capillary forces are reduced along with the observed contact angle hysteresis.

FIGURE 6: Effect of Mat Thickness - Water Contact Angle of 25% PS Mats

FIGURE 7: Effect of Mat Thickness - Hysteresis of 25% PS Mats
3.3 Magnetic Particle Embedded in Polystyrene Fiber

Magnetic composite fibers, in which magnetic nanoparticles are embedded into a polymeric fiber matrix, have been previously fabricated and proven to exhibit many interesting mechanical behaviors under the influence of magnetic fuel. This material offers a wide range of potential applications such as electromagnetic interference shielding, biomedical sensing, magneto-optical storage etc. The experiment herein explores the possibilities of fabricating PS/Iron magnetic composite fibers that have magnetic field-dependent properties of superhydrophobicity and hysteresis.

PS solutions at two different concentrations (10% and 25%) were mixed with the same weight of Iron nanoparticles. The mixtures were then sonicated for 90 minutes to ensure the separation of particles. The sonicated PS solutions of 10% and 25% were then electrospun onto glass substrates for 10 minutes and 5 minutes, respectively to produce PS-Iron composite fiber mats. The morphologies of the composite mats were studied using SEM as shown in Figure 8.a to 8.c below.
FIGURE 8a: Close-up of a magnetic particle embedded fiber

FIGURE 8b: 10% PS fiber with embedded particles

FIGURE 8c: 25% PS fiber with embedded particles
The majority of the magnetic particles were found to be embedded within the PS fibers and do not appear clearly in the SEM images. The magnetic particles were added at the same weight as the PS. Therefore, after solvent evaporation, the resulting mats should consist of 50% PS and 50% iron by weight. TGA was performed on the samples and the results confirmed that the magnetic particles were embedded inside the PS fibers. Figure 9 show microscope images of a composite mat before and after PS removal illustrating the relatively uniform dispersion of the iron particles within the fibers.

It must be noted that pure PS fiber mats (with no Iron particle embedded) were also tested for water contact angle and hysteresis under the influence of magnetic field. Results of this quick experiment showed that the water contact angle and hysteresis properties of the pure PS fiber mats remain consistently the same regardless the application of magnetic field. Therefore the embedded nanoparticles inside the magnetic fiber can be assumed to be responsible for the observed change in water contact angle and hysteresis properties of the magnetic fiber mats with the application of magnetic field.
FIGURE 9: Microscopic Image of a Composite Mat before and after TGA

Figures 11 and 12 show the water contact angle and hysteresis measurements of the 10% and 25% PS/Iron composite samples with and without the application of a magnetic field and for two different types of permanent magnets (rare earth bar magnet and horseshoe). The measurements were repeated multiple times to ensure statistically-significant reproducible results and the error bars in the data were calculated from the statistics of the measurement set. The results show that the externally applied magnetic
field increases the water droplet contact angle by up to 10 degrees for both fiber diameters and for both types of magnets. Figure 10a and 10b show the examples of the measurements of water contact angle and hysteresis, respectively, with and without magnet. The results also show that the magnetic field reduces the water droplet contact angle hysteresis by a similar amount, but only for the bar magnet. The horseshoe magnet did not have a statistically significant effect on the contact angle hysteresis at either polymer concentration. We do not have quantitative data on the relative strength of the two magnets and our contact angle apparatus made it very difficult to vary the magnet position to affect field strength and orientation. The bar magnet is qualitatively stronger than the horseshoe magnet and we believe that the absence of a statistically significant change in the contact angle hysteresis with the horseshoe magnet is most likely due to the weaker magnitude of the applied field.
FIGURE 10a: Water Contact Angle Images of Magnetic Particle Embedded in Polystyrene Fiber - Without and With Magnetic Field

WITHOUT MAGNET

WITH MAGNET

FIGURE 10b: Hysteresis Images of Magnetic Particle Embedded in Polystyrene Fiber - Without and With Magnetic Field

NO MAGNET

WITH MAGNET
We believe that the observed increase in water droplet contact angle in the presence of a magnetic field is due to a field-induced increase in the surface roughness factor. That is, the magnetic field is physically moving the fibers and changing the surface morphology. The magnetic fabrics could, for example, be lifted off of a surface by the magnet. However, SEM imaging could not be performed in the presence of the magnet and attempts to visualize the field-induced morphology changes using optical microscopy were inconclusive due to insufficient resolution.
The results show conclusively that the hydrophobicity of electrospun PS/Fe magnetic fabrics can be adjusted through the application of an externally applied magnetic field. The externally applied field modifies both the contact angle as well as the contact angle hysteresis (stickiness) of the magnetic fabric. For the surfaces studied in this work, the applied magnetic field was found to increase the hydrophobicity and decrease the stickiness. Small, permanent magnets with limited strength were used in this study to qualitatively demonstrate the effect of magnetic field on the hydrophobicity of magnetic fabrics. We believe that, by optimizing the fabric properties and by using stronger electromagnets with tunable strength and field orientation it may be possible to develop smart fabrics with externally adjustable wettability.
Magnetic fabrics consisting of iron nanoparticles embedded within polystyrene fibers were produced using electrospinning. The magnetic fabrics were tested with and without an externally-applied magnetic field. The results show that the magnetic field increases the hydrophobicity of the surface and decreases the contact angle hysteresis (a measure of the stickiness of the surface). The underlying mechanism responsible for the observed changes in hydrophobicity with magnetic field are currently unclear, but are consistent with either an increase in surface roughness or a decrease in surface free energy.
Literature Cited
