SUPERHYDROPHOBIC BEHAVIOR OF ELECTROSPUN NANOFIBERS WITH VARIABLE ADDITIVES

A Thesis by

Muhammet Ceylan

Bachelor of Science, Ataturk University, 2006

Submitted to the Department of Mechanical Engineering
and the faculty of the Graduate School of
Wichita State University
in partial fulfillment of
the requirements for the degree of
Master of Science

December 2009

© Copyright 2009 by Muhammet Ceylan

All Rights Reserved

SUPERHYDROPHOBIC BEHAVIOR OF ELECTROSPUN NANOFIBERS
WITH VARIABLE ADDITIVES

The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science with a major in Mechanical Engineering.

_____
Ramazan Asmatulu, Committee Chair

_____
T. S. Ravigururajan, Committee Member

_____
Bayram Yildirim, Committee Member

DEDICATION

To my family, my friends and my professors

ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude to my advisor, Dr. Ramazan Asmatulu, who supervised the work presented in this thesis from the beginning, and also guided me toward the successful completion of this thesis. I appreciate his guidance throughout my graduate study at Wichita State University.

I would also like to acknowledge my thesis committee, Dr. T. S. Ravigururajan and Dr. Bayram Yildirim, whose suggestion has been very useful in directing my research.

Special thanks to Saadet Ceylan for her support and encouragement throughout my Master's degree. I would like to thank great friends that I have at the Research Group under Dr. Asmatulu at Wichita State University for their guidance in my research work and thanks to all my friends who stood by me at all times.

I enlarge my gratitude to my parents, Temel Ceylan and Ayten Ceylan also my brothers Mustafa, Ahmet Serkan and Mahmut without their constant support and encouragement this day would not be possible. Whenever I needed guidance and support, they were always there for me. I cannot thank them enough for their immeasurable support and guidance.

ABSTRACT

This report presents the hydrophobic (90<θ<150) and superhydrophobic (150<θ<180) behaviors of electrospun fibers in the presence and absence of various inclusions. The research on superhydrohobicity has accelerated around the globe and many researchers have been taking keen interests in fabrication of superhydrophobic materials, using several methods, such as sol-gel, vapor deposition, plasma treatment, surface etching and layer by layer assembly. In the present research, polystyrene (PS) and polyvinyl chloride (PVC) fibers with diameters between 200 nm and 7.60 µm were fabricated by electrospinning technique, and then surface morphology and superhydrohobicity of these electrospun nanofibers were investigated. The results indicate that the water contact angle of the nanofiber surfaces goes up to 165 ° based on the fiber diameter, type of materials and surface porosity/roughness. Additives such as graphene, surfactant and titanium dioxide (TiO_2) nanoparticles (nano powders) ranging from 10-25 nm were added into the same polymers (PVC, PS) and investigated to determine their performances. Both heat treatment and surface treatment were also applied to the fabricated fibers. The results with the additives indicate that the water contact angle is even further increased up to 178°. This may be because of the nanoscale voids (entrapped air) in the pores and surface energy of the nanofiber surface. These higher contact angle nanomaterials can have various industrial applications, such as non-wettable fabric, antibacterial surface, low friction devices, MEMS, NEMS, microfluidics and nanofluidics.

TABLE OF CONTENTS

Chapter Page

1. INTRODUCTION 1

2. BACKGROUND AND LITERATURE REVIEW 4

2.1 History of Electrospinning 4
2.2 Electrospinning Process 7
2.3 Mathematical Model for Initiation of Jet 9
2.4 Effects of System and Processing Parameters on Electrospun Fibers 11
2.4.1 System Parameters 12
2.4.2 Process Parameters 13
2.5 Properties of Nano-Fibers 14
2.6 SEM Characterization of the Electrospun Fibers 15
2.7 Sol-Gel Process 15
2.8 Hydrophobicity and Superhydrophobicity*** 18
2.9 Theory of Contact Angle 18

3. EXPERIMENTAL 21

3.1 Materials: 21
3.2 Polyvinyl Chloride 21
3.3 Polystyrene 23
3.4 Surfactant 24
3.5 AFM Characterization 25
3.6 Method 27

4. RESULTS AND DISCUSSION 35

4.1 Superhydrophobic Behavior of Electrospun Micro and Nanofibers 35
4.2 Superhydrophobic Behavior of Electrospun PVC Nanofibers with Graphene Inclusion 37
4.3 Superhydrophobic Behavior of Electrospun PS and PVC Fibers with TiO2 Nanoparticles 39
4.4 Heat Treatment Effects on Superhydrophobici Behavior of Electrospun Fibers 42
4.5 Superhydrohobic Behavior of Electrospun Fibers with Surfactant Treatment 49

5. CONCLUSION 52

REFERENCES 53

LIST OF TABLES

Table Page

Table 4-1 : Contact angle values of various size PS and PVC fiber films..... 36

Table 4-2: Contact angle values of various size nano graphene into PVC fiber films. 38

Table 4-3 : Contact angle values of various size TiO_2 nanoparticles into PS and PVC fiber films. 41

Table 4-4 : Contact angle values of PS fibers obtained at varying temperatures. 45

Table 4-5 : Water contact angle values of PVC fibers obtained at various temperatures. 47

Table 4-6: Water contact angle value of PVC nanocomposite fibers obtained at various temperatures. 49

Table 4-7 : Contact angle values of PVC nanocomposite fibers obtained at various weight percentages of surfactant solutions. 51

TABLE OF FIGURES

Figure Page

Figure 1-1 : A schematic illustration of an electrospinning process..... 2

Figure 1-2 : Water contact angle values of superhydrophobic (left), hydrophobic and hydrophilic surfaces. 3

Figure 2-1: A schematic illustration of an electrospinning process. 8

Figure 2-2: Viscoelastic dumbbells showing a segment of the rectilinear portion of the jet..... 9

Figure 2-3 : Schematic representation of water contact angle on a solid surface. 19

Figure 2-4 : Drawings of the water droplet on a solid surface (left), and its Wenzel and Cassie-Baxter states. 20

Figure 3-1: Polyvinyl Chloride (PVC)..... 22

Figure 3-2: Polystyrene (PS) granules in a plastic cup 24

Figure 3-3 : TiO_2 cluster particle size of 59nm measured by AFM..... 26

Figure 3-4 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), d=25cm, v=25kv m=2.5ml/hr). 28

Figure 3-5 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), d=15cm, v=15kv m=4ml/hr). 28

Figure 3-6 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 0.5%Graphene d=30cm, v=25kv m=1.5ml/hr). 29

Figure 3-7 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 1%Graphene d=30cm, v=25kv m=1.5ml/hr). 29

Figure 3-8 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 1% TiO_2 d=25cm, v=25kv m=1ml/hr). 30

Figure 3-9 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 2% TiO_2 d=25cm, v=25kv m=1ml/hr). 30

Figure 3-10 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 4% TiO_2 d=30cm, v=25kv m=1ml/hr). 31

LIST OF FIGURES (continued)

Figure .....Page

Figure 3-11 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 8% TiO_2 d=30cm, v=25kv m=2.5ml/hr). 31

Figure 3-12 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 2% TiO_2 d=30cm, v=25kv m=1.5ml/hr). 32

Figure 3-13 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 4% TiO_2 d=30cm, v=25kv m=1.5ml/hr). 32

Figure 3-14 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 8% TiO_2 d=30cm, v=25kv m=2.5ml/hr). 33

Figure 3-15 : Photograph showing the electrospun nanofibers on the grounded collector. 33

Figure 3-16: Contac angle measurement goniometer set up (CAM 100). 34

Figure 4-1 : SEM images of PVC (left) and PS electrospun fibers obtained at 2.5 ml/hr pump speed, 25 kV DC voltage and 25 cm spinning distance. 35

Figure 4-2 : Water contact angle values of PVC (above) and PS fibers obtained at 2.5 ml/hr pump speed, 25 kV DC voltage and 25 cm spinning distance. 36

Figure 4-3 : Water contact angle values of PVC fibers (PVC&DMAC 80:20), 0.5%Graphene (d=30cm, v=25kv, m=1.5ml/hr)obtained a, 1%Graphene b, 2%Graphene c, 4%Graphene d. 37

Figure 4-4 : Water contact angle values of PS nanocomposite fibers (PS&DMF 80:20), 1% TiO_2 (d=25cm, v=25kv, m=1ml/hr)obtained a, 2% TiO_2 b, 4% TiO_2 c, 8% TiO_2 d..... 39

Figure 4-5 : Water contact angle values of PVC nanocomposite fibers (PVC&DMAC 80:20), 1% TiO_2 (d=25cm, v=25kv, m=1ml/hr) obtained a, 2% TiO_2 b, 4% TiO_2 c, 8% TiO_2 d.40

Figure 4-6: Water contact angle values of PS fibers (PS&DMF (80:20), d=20cm, v=20kv m=3ml/hr)obtained at 60 ºC a, 80 ºC b, 100 ºC c and 120 ºC d. 42

Figure 4-7: A Water contact angle value of PS fibers (PS&DMF (70:30), d=20cm, v=20kv m=3ml/hr) obtained at 60 ºC a, 80 ºC b, 100 ºC c and 120 ºC d 43

Figure 4-8: Water contact angle values of PS fiber (PS&DMF (60:40), d=20cm, v=25kv m=3ml/hr) obtained at 60ºC a, 80 ºC b, 100 ºC c and 120 ºC d. 44

LIST OF FIGURES (continued)

Figure .....Page

Figure 4-9 : Water contact angle values of PVC fibers (PVC&DMAC (80:20), d=25cm, v=25kv m=1ml/hr) obtained at 60 ºC a, 80 ºC b, 100 ºC c, and 120 ºC d. 46

Figure 4-10 : Water contact angle values of PVC nanocomposite fibers(PVC&DMAC (80:20), d=30cm, v=25kv m=1.5ml/hr) obtained at 60 ºC heat treatment and 0.5%Graphene a, 80 ºC and 1%Graphene b, 100ºC and 2% Graphene c, and 120ºC and 4%Graphene d. 48

Figure 4-11 : Water contact angle values of PVC nanocomposite fibers (PVC&DMAC (80:20), solution d=30cm, v=25kv m=1.5ml/hr) obtained at 1% graphene into 0.25% Organoalkoxysilane a, 0.5% graphene into 0.5% surfactant solution b, 2% graphene into 1% surfactant solution c, and 4% graphene into 1% surfactant solution d. 50

LIST OF ABBREVATIONS

PVC	Polyvinyl Chloride
PS	Polystyrene
DMF	Dimethylformamide
DMAC	Dimethylacetamide
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
TiO_2	Titanium dioxide

LIST OF SYMBOLS

µ	Micron
^{o}	Degree
nm	Nanometer
mm	Millimeters
µm	Micrometer
pH	Power of Hydrogen

1. INTRODUCTION

In this project, electrospinning process was used to produce micro and nanofibers to measure surface hydrophobic behaviors of those electrospun fibers. In electrospinning, a high DC voltage or high electric field is used to overcome the surface tension of the polymeric solution. When the intensity of the electric field is increased more than a certain limit, called threshold intensity, the hemispherical surface of the polymer solution at the tip of the capillary tube begins to elongate in a structure known as Taylor cone [1-3]. A jet travels in a straight path, which is commonly referred to as the jet length in which, instability occurs. This causes huge stretching of the fiber to form micro and nanoscale fibers. During this process, solvent in the electrospun fibers evaporates to form solid fibers. The diameter of fibers depends on parameters, such as viscosity, concentration, applied voltage, pump speed and syringe to screen distance [4]. Figure 1-1 shows the electrospinning of a polymeric solution [5]. In this experiment, fibers with different diameters were produced and effects of water contact angles on those fibers were investigated.

Figure 1-1 : A schematic illustration of an electrospinning process [5].

Hydrophobicity refers to the physical property of a surface on which hydrophobic molecules repel water molecules, which causes higher water contact angles, θ, (over 90°). In another word, water adsorption on the surface is thermodynamically impossible. Hydrophobic (hydro – water, phobic – fearing) molecules can be non-polar natural and synthetic materials, such as alkanes, oils, fats and greasy substances [6-9]. However, hydrophilicity is exactly the opposite of hydrophobicity, where polar hydrophilic surface interacts with water molecules through hydrogen bonds. This creates lower water contact angles (lower 90°). Some of the materials can show both hydrophobic and hydrophilic parts on the surface. For example, soap is a surfactant that has a hydrophobic tail and hydrophilic head groups on it, which allows it to dissolve in both water and oil depending on the orientations of the surfactant molecules [6, 7].

Superhydrophobicity is a physical property of a surface where water contact angle exceeds 150°. A water droplet can bounce on the superhydrophobic surface and also can roll-off with less than 10° contact angle. Because of the surface roughness and hydrophobicity of the solid surfaces, superhydrophobic surface has an extremely high water repellent behavior, which makes it very difficult to wet. It is also called a self-cleaning surface [7]. Thus, bacteria, fungi, algae and other parasites and microorganisms cannot grow on top of the superhydrophobic surfaces. Superhydrophilicity is the opposite of superhydrophobicity, in which water contact angle becomes less than 5° in 0.5 sec or less. Superhydrophilic materials have several advantages, such as antifogging, antibacterial, heat transfer, higher rate filter media, fuel cells and other wettable surfaces [10, 11]. Figure 1-2 shows the water contact angle values of superhydrophobic [12], hydrophobic [13] and hydrophilic [14] surfaces.

Figure 1-2 : Water contact angle values of Superhydrophobic (left), hydrophobic and hydrophilic surfaces [12, 13, 14].

2. BACKGROUND AND LITERATURE REVIEW

2.1 History of Electrospinning

Electrospinning has been of interest of many decades Willim Gibert [15] determined that a spherical drop of water could be drawn into conical shape when an electrical charge is applied. This idea was proposed 370 years ago. This was beginning of electrospinning process [16]. Lord Rayleigh [16, 17, 18] discovered the instability mechanism of the electrified liquid jet with and without electrostatic field. In1882, he found out the instability mechanism in electrified liquid jet and showed that electrostatic force overcomes surface tension. Which acts in the opposite, direction and a charged jet emerges [16]. In 1960, Taylor [19, 20, 21] studied the disintegration of water drops, and explained that a conical interface between two could not exist in equilibrium state in an electrostatic field. It was discovered that the droplets have enlarged or elongated at the onset of instability and formed a conical shape that had a semi-vertical angle of 49.3 degrees. This is the first proposition that Taylor cones can be utilized for controlling and predicting properties, which has been discussed broadly by later researchers around the globe [16].

The process of electrospinning of polymeric solution has been well known since 1930's [22, 23]. There are several patents by Formhals [22, 24] pertaining to process and experimental set-up and their applications. In 1971, Bumgarten [25] fabricated the first polymer fiber by electrospinning. He electrospun acrylic fibers in micro size and developed a relation between fiber diameter and solution viscosity. In 1981, Larrondo and Manley studied the relationship between the melt temperature and the fiber diameter of polyethylene and polypropylene. He determined that the fiber diameter decreased by increasing the melt temperature. In 1987, Hayati

studied the effects of electrostatic field, process parameters and process conditions on electrospun fibers. Hayati stated that the conducting polymeric solution with a high-applied electrostatic field produced an unstable jet that followed spiral and looping motion. In 1994, Reneker and Doshi [26, 27], studied the electrospinning of polyethylene oxide (PEO). Reneker and Srinivasan [28, 29] electrospun poly(aniline) in sulfuric acid. Debatably, the most usable electrospinning processes where developed in 1995s. When Reneker and coworkers started publishing several papers on electrospinning process, and its potential applications.

In 1995, Reneker and Chun [30, 31] used electrospinning technique to produce Nano-fibers from polymeric solutions of Poly (amic acid) and Poly (acrylonitrile). G.J. Vancso [32, 33], in 1996, electrospun poly (ethylene oxide) and used scanning probe microscopy to study the surface morphology of fibers. Reneker and Feng [34, 35], in 1997, used polymeric solution of nylon 6 and polyimide to produce nanofibers by electrospinning. Reneker and Kim [36, 37] electrospun polybenzimidazole nanofibers and studied the reinforcement effects on electrospun nanofibers in a rubber and epoxy matrix. Fabric membranes were electrospun at US Army research laboratory (Aberdeen) [38]. A silicone polyester composite vascular graft was produced by electrospinning technique by Stenoien [39], in 1998. Shahrzad Zakoob [40, 41] used electrospinning technique to fabricate silk nanofibers and matched them with natural silk fibers. Elliot L. Chaikof and coworkers [42], in 1999, established the electrospinning of synthetic elastin-mimetic peptide. Reneker and Fong [32, 36, 43, 44] produced the beaded structure of nanofibers by electrospinning using the polymeric solution of poly (ethyleneoxide).

In 1999, MacDiarmid [45], produced a conducting electrospun mat from polymeric solution with a mixture of conducting material. In this process, he used polyaniline as a conducting polymer and doped it with poly (ethyleneoxide) and camphorsulfonic acid. The

conductivity of the electrospun mat was found to be lower than the cast film, due to porosity effects in the fiber texture. Jong-Sang Kim [46] studied the thermal characterization of electrospun polynaphthalene terephthalate, polyethylene terephthalate, polyester and polyethylene terephthalate-co-polynathalene terephthalate. Greiner [47, 48] electrospun polylactide from organic solution and added organosoluable salt and found that the fiber diameter was reduced.

In 2001, F. Ko used carbon nanotubes to produce composite nanofibers. G. Chase [49] incorporated glass fibers with nylon and polyacrylonitrile polymeric solution and produced composite nanofibers. Electrospinning of biodegradable polymers and biopolymers is of interest by many researchers, and some very promising results were published by Bowlin [50] on electrospinning of collagen, and their use as a band-aid. Several patents on biomedical applications are reported in recent years; prominent amongst them is the one reported by Renekar and coworkers [51], wherein they fabricated skin mask by directly electrospinning fibers on the skin. Another research was conducted by P. Gibson [52] where he reported the production of electrospun fibers containing pH adjustment substances for use in wound dressing. In 2003, poly (ethylene terephthalate-co-ethylene isophthalate copolymers, poly (hexyl isocyanate), cellulose, poly (3, 4 ethylenedioxythiophene) and acrylonitrile-butadiene-styrene were electrospun from different polymeric solutions [16]. Electrospinning technology has been used for enzymes preservation and chemical warfare protective clothing. Recently, Fang [53] has reported the ability of electrospinning using multiple syringes thus increasing the production of nanofibers.

In this modern era, electrospinning technique draws attention by many researchers and scientists around the globe. This attention is increasing every year. A sudden rise in research on electrospinning is due to latest knowledge of industrial applications of nanofibers. Several

companies such as Donaldson, Espin, Star and Nanomatrix are applying this technology to produce nanofibers.

2.2 Electrospinning Process

Electrospinning uses an electrical charge to form a mat of micro or nanosize polymeric fibers [1]. In a electrospinning process, an electric potential is utilized to create an electrically charged jet of polymer solution or melt, which dries or solidifies to leave a nanoscale polymer fiber on a specified surface. One electrode is placed into the spinning solution, and the other is attached to a grounded surface where the fibers are collected. Electric voltage is applied to the end of a capillary tube that consists of the polymeric solution held by its surface tension. Charge repulsion causes tangential forces directly opposite to the surface tension of the polymer, which needs to overcome to form fibers. When the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape called the Taylor cone [54]. By increasing electric field, a critical value is achieved as a repulsive electrostatic force that overcomes the surface tension, and a charged jet of fluid emerges from the tip of the Taylor cone [54]. The jet of the discharged polymer solution undergoes a drying process in the air where the solvent evaporates, and leaves behind a charged polymer fiber. Then lays itself randomly (non-woven) on a grounded collecting metal screen. At the end of the spinning process, the discharged jet totally solidifies in a few hours, and then is collected on the grounded surface [1, 55-59]. Thus, the resultant product is a nanoporous non-woven nanofiber film, which can be used for various applications because of its higher surface area and higher aspect ratio [54,76-81]. Figure 2-1 shows a simplified schematic of the electrospinning process and resulting electrospun polymeric fibers [60].

Figure 2-1: A schematic illustration of an electrospinning process.

Nanofibers are of great interest because of the extreme small sizes. Diameters of nanofibers are generally in the range of 10 nm to 500 nm and these nanofibers can be made from a wide variety of polymeric solutions. Nanosize particles can be encapsulated in polymeric solution during electrospinning to produce nanofiber composites [76-81]. The surface area of the electrospun fibers is 3-5 orders of magnitude higher than the conventional fibers, for instance fiberglass, mineral wool, polymeric fibers/cloths, open cell foam and wood fibers. With higher surface area to volume ratios, flexibility and high aspect ratio, nanofibers offer a wide variety of applications, and because of that research and development in these materials have been accelerated for over a decade [1, 55].

Some of the significant applications of the nanofibers include (but are not limited to) air and liquid filtration, high frequency antenna, photonics catalytic substrates, drug delivery, protective clothing, cell scaffolding, sound absorption and wound healing. Different applications require different nanofiber properties, so based on the properties, such as mechanical strengths,

hydrophobicity / hydrophilicity, stiffness and biodegradability / biocompatibility, flame resistance and flexibility, material use can vary [3, 56-58].

2.3 Mathematical Model for Initiation of Jet

Renekar et al [61, 62] proposed a mathematical model to describe the whipping or chaotic motion of the jet also known as the bending instability of the jet. The bending instabilities can be thought as a system of connecting viscoelastic dumbbells. Consider a rectilinear liquid jet in an electrostatic field emerging from the capillary tube parallel to its axis. We can model a segment of the electrified jet by a viscoelastic dumbbell as shown in Figure 2-2 [61, 62].

Figure 2-2: Viscoelastic dumbbells showing a segment of the rectilinear portion of the jet [54].

The beads, A and B possess a charge “e” and a mass “m”. Suppose the position of bead A is fixed by the non- coulomb forces. The coulomb repulsive force acting on bead B is $-e^2/I^2$. “I” is the filament length. The force applied on B due to the electrostatic field is –e E/H, where “E” is the applied field and ”H" is the distance from the pendent drop to the collector. The dumbbell,

AB, represent a model of viscoelastic Maxwellia jet. Therefore, the stress, σ, pulling back B to A can be given by [61, 62],

$$\frac{d\sigma}{dt} = \frac{Gdl}{ldt} - G.\frac{\sigma}{\mu} \tag{2.1}$$

Where “t” is the time, “G” and “μ” are the elastic modulus and viscoelasticity, respectively. The momentum balance for bead B can be given by [61, 62]

$$\frac{mdv}{dt} = -\frac{e^2}{l^2} - e.\frac{E}{h} + \sigma\beta^2\pi \tag{2.2}$$

where "β" is the cross-sectional radius of the filament, “v” is the velocity of bead B that satisfies the kinematics equation [61, 62].

$$\frac{dt}{dv} = -v \tag{2.3}$$

Based on the experimental observations, several mathematical models have been developed to investigate the electrospinning process. Reneker and co-workers took the charged liquid jet as a system of connected, viscoelastic dumbbells and provided an interpretation for the formation of bending instability [63, 64]. They calculated the three –dimensional trajectory for the jet using a linear Maxwell equation and the computed results were in agreement with experimental results. Rutledge and co-workers treated the jet as a long, slender object and

thereby developed a different model to explain the electrospinning process [65]. Their experimental and theoretical studies reveal that the electrospinning process involves whipping instability of a liquid jet. The whipping instability is mainly caused by electrostatic interactions between the external applied field and surface charges on the jet. The fiber formation in nano-size is due to the stretching and accelerating fluid filament in the instability zone. They also showed that the model could be extended to predict the saturation of whipping amplitude, and the diameter of the resulting fibers [66]. Feng proposed another model to show the motion of a highly charged jet in an electrostatic field, and the role of non-Newtonian rheology in the stretching of an electrified jet was examined [67]. All these models provide a better understanding of the electrospinning process with their limitations.

2.4 Effects of System and Processing Parameters on Electrospun Fibers

There are two types of parameters that affect the morphology of electrospun nanofibers including system parameters and process parameters. These parameters are described below.

- System Parameters:
    1. Polymer and solvent types
    2. Viscosity, conductivity and surface tension of polymers

- Process Parameters:
    1. Electric potential, flow rate and polymer concentration
    2. Distance between the capillary and collection screen
    3. Temperature, humidity, and air velocity effects in the chamber

2.4.1 System Parameters

2.4.1.1 Polymer and solvent types

Some of polymers can be electrospun in different solvents. The polymer for electrospinning should have moderate molecular weight. If the molecular weight is too high, then electrospinning will be very difficult. If it is too low, electrospinning will result in spherical and beaded structures. The solvent should be such that it can dissolve polymer easily.

2.4.1.2 Viscosity, conductivity and surface tension of polymers

Viscosity plays a major role in electrospinning. It has significant influence on the electrospun fiber diameters. If the viscosity is too high, electrospinning sometimes becomes impossible. A high viscosity results in large fiber diameter. Beads and pores are not formed when the viscosity is high. As the viscosity of the polymeric solution increases, the hemispherical shape at the apex of the capillary tubes changes to conical shape. The diameter of the fiber increases as the viscosity increases. The solution should be conductive. If it is non-conducting, calcium chloride may be added to make it conductive. When the conductivity of the solution is high, the fiber diameter is low. For having fiber diameter at nano range, the conductivity of the polymeric solution should be high. Beads and pores are observed, when the conductivity of the solution is low. When the surface tension of the polymeric solution is low, nanofibers without beads or pores can be obtained. Surface tension should not be too low or too high for electrospinning, but should be a compromise between the two for having fibers at nano range.

2.4.2 Process Parameters

2.4.2.1Electric potential, flow rate, polymer concentration and molecular weight

The jet diameter is reduced as it progresses to the target, because the solvent is evaporating and the fiber is continuous stretching caused by the jet electrostatic forces. The fiber diameter decreases as the applied electrical potential increases. An increase in the applied electrical potential increases the field strength, which in turn accelerates changes in the electrified jet and instability region. This will result, in producing fibers that are sub-micron size. The drift velocity of the charge carriers is related to mobility of charge carriers by the following equation [68].

$$u = m_0 V \tag{2.4}$$

where “u” is the drift velocity, "m_0" is the mobility of charge carriers and "V" is the applied field. The morphology of the fibers depends upon the flow rate of the solution. When the flow rate is in excess, fibers are obtained with defects such as beads and pores. The polymer concentration should be a compromise between minimum and maximum. If the polymer concentration is too high, a beaded structure is obtained. The diameter of electrospun fibers increases as the polymer concentration increases. The shape of the beaded structure changes from spherical to spindle, when the polymer concentration increases. Higher polymer concentration (higher viscosity), will result in large fiber diameter. When the molecular weight is high, viscosity will be high and electrospinning will result in beaded structure.

2.4.2.2Distance between the capillary and collection screen

The fiber diameter reduces as the distance between capillary and collection screen increases. When this distance is too small, we observe some beaded structure.

2.4.2.3Temperature, humidity, and air velocity effects in the chamber

Electrospinning process is usually carried out at room temperature under normal conditions. However, if the temperature is little above the room temperature, the evaporation rate will be high, and this will help in reducing the fiber diameter. Increased humidity will reduce fiber diameter to some extent. High airflow will increase the evaporation rate due to convection and will help in reducing fiber diameter.

2.5 Properties of Nano-Fibers

1. High Aspect ratio
2. Nano- size diameter with high surface area
3. Good surface morphology
4. Large surface area to volume ratio
5. Thermally and chemically stable
6. Low ohmic resistance
7. High porosity
8. High directional strength
9. Flexibility
10. Biocompatibility and biodegradability

2.6 SEM Characterization of the Electrospun Fibers

When the filament in the electron gun is sufficiently charged, it emits electrons, which are focused onto the sample surface using a series of lenses. The sample surface when struck with these electrons emits secondary electrons which when detected by the scanner the sample topography is reproduced and the SEM image is formed. SEM uses electrons that are emitted from the specimen to reconstruct the image. The operating conditions of the SEM are accelerating voltage of 10Kev, Spot Size of 4, and a work distance of 12 mm. Images are taken at various magnifications and across various areas for each sample. Resolution can easily go below 10 nm.

2.7 Sol-Gel Process

Development in the sol-gel processing of ceramics and glass materials started early 1800s with Ebelman, and Graham's studies on silica gels. There is great potential for achieving high levels of chemical homogeneity in colloidal gels. The sol-gel process in the mid-1900s was used to produce a large number of novel ceramic oxide compositions, involving Ti, Al, Zr and Si that could not be made using traditional ceramic powder processes. The final diameter of the spherical silica powder depends upon the initial concentration of ammonia and water, the kind of silicon alkoxide (esters, pentyl, ethyl, and methyl) and alcohol (butyl, methyl, pentyl, and ethyl) blend used, and temperature of the reactant. Sugimoto and Overbeek discovered that nucleation of particles in a short time followed by growth with no supersaturation will yield monodispersed colloidal oxide particles. Matijevic and co-workers worked on these concepts to fabricate colloidal powders with controlled dimensions and morphologies, counting oxides $(Fe_3O_4, TiO_2, \alpha - Fe_2O_3, CeO_2)$ carbonates, hydroxides, metals, and sulfides.

Three approaches are used to make sol-gel monoliths: *method 1*, gelation of a solution of colloidal powders; *method 2*, hydrolysis and polycondensation of alkoxide or nitrate precursors followed by hypercritical drying of gels; and *method 3*, hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient atmospheres. Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100 nm. All the steps for sol-gel are given below:

Step 1 Mixing: In method 1 a suspension of colloidal powders, or sol, is formed by mechanical mixing of colloidal particles in water at a pH that prevents precipitation. In methods 2 and 3 a liquid alkoxide precursor, such as $Si(OR)_4$ where R is CH_3, C_2H_5, C_3H_7, is hydrolyzed by mixing with water.

Step 2 Casting: The sol is a low-viscosity liquid, it can be cast into a mold. The mold has to be selected to avoid adhesion of the gel.

Step 3 Gelation: With time the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend significantly upon the size of particles and extent of cross-linking prior to gelation.

Step 4 Aging: Aging of a gel called syneresis, involves maintaining the cast object for a period of time, completely immersed in liquid. Throughout aging, polycondensation continues along with localized solution and reprecipitation of the gel network, that increases the thickness of inter particle necks and decreases the porosity. The strength of the gel thereby increases with aging. An aged gel must develop enough strength to resist cracking during the drying.

Step 5 Drying: Throughout drying the liquid is removed from the interconnected pore network. Capillary stresses can build up during drying when the pores are small (<20 nm). Because of these stresses the gels are going to crack catastrophically unless the drying process is controlled by decreasing the liquid surface energy by addition of surfactants or elimination of

very small pores (method l), by hypercritical evaporation, which avoids the solid-liquid interface (method 2), or by obtaining monodispersed pore sizes by controlling the rates of hydrolysis and condensation (method 3).

Step 6 Dehydration or Chemical Stabilization: The removal of surface silanol $(Si-OH)$ bonds from the pore network results in a chemically stable porous solid. Porous gel-silica made in this manner by method 3 is optically transparent with interconnected porosity and has sufficient strength to be used as optical components when impregnated with optically active polymers such as fluors, wavelength shifters, dyes, or nonlinear polymers.

Step 7 Densification: Heating the porous gel at high temperatures causes densification to occur. The pores are eliminated, and the density ultimately becomes equivalent to fused quartz or fused silica [69].

TiO_2 nanosize particles are used for industrial applications, for instance pigments, cosmetics, catalysts, catalyst supports, and electronic devises and so on. Fine TiO_2 nanoparticles received significant interest for their high photo catalytic activity, and are applied for environmental purification, and antibacterial purposes. Currently, they are also applied for dye-sensitized solar cells to improve the various functions; morphological control as well as the conventional powder refinement [2].

2.8 Hydrophobicity and Superhydrophobicity

Hydrophobicity refers to the physical property of a surface on which hydrophobe molecules repel water molecules, causing higher water contact angles, θ, (over 90°). In another word, hydrophobic means a surface that water does not spread on it and thermodynamically is unstable. The water stands up in the form of drops on and a contact angle can be measured from plane of the surface. Superhydrophobicity is a physical property of a surface where a water contact angle exceeds 150°. Hydrophobic (hydro – water, phobic – fearing) molecules can be non-polar natural and synthetic materials, such as alkanes, oils, fats and greasy substances.

This following effect may tend to increase the apparent contact angle to a greater value than the true one. Surface roughness may be enhanced by the repellent coating [74] and additives such as graphene, TiO_2 as well as varying the parameters of electrospinning. When the true contact angle is larger than 90°, then the angle can be increased by the roughness. According the Wenzel relation:

$$\cos\theta_{app} = R\cos\theta_{true} \tag{2.5}$$

where R is the ratio of actual to projected area. Of course, if θ is less than 90°, roughness appears to enhance wetting [70].

2.9 Theory of Contact Angle

In 1805, Thomas Young defined the theory of contact angle, θ, by analyzing the three acting forces on a surface of water droplet surrounded by air. Based on the Young's definition, the process of a water droplet standing on a surface may be shown in Figure 2-3 at which the droplet stays on the solid surface and orients through air with a contact angle. The equilibrium

between the three interfacial energies can be expressed by Young`s equation associated with the contact angle [6,7]:

Figure 2-3 : Schematic representation of water contact angle on a solid surface.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \tag{2.6}$$

at which γ_{SG} is interfacial tension between the solid and gas, γ_{SL} is interfacial tension between the solid and liquid, and γ_{LG} is interfacial tension between the liquid and gas. Wenzel determined that when the liquid is in intimate contact with a microstructured surface, θ will change to Wenzel contact angle θ_W* [6,7]:

$$\cos\theta_W * = r\cos\theta \tag{2.7}$$

where r is the ratio of the actual area to the projected area. The Wenzel's equation reviles that surface microstructures play important roles on hydrophobicity of the surfaces, and have always the natural tendency of the surface. Another words, in the Wenzel approach, hydrophobic surface becomes more hydrophobic if the surface microstructures are changed (or rougher and more voids), where new contact angle becomes greater than the original one. Conversely, hydrophilic surface becomes more hydrophilic, or the new contact angle of hydrophilic surface becomes less than the original value.

Cassie and Baxter found that if the liquid is suspended on the tops of highly propos microstructures, θ will change to θ_{CB} * [6,7]:

$$\cos\theta_{CB}^{*} = \varphi(\cos\theta + 1) - 1 \tag{2.8}$$

where φ is the area fraction of the solid that interacts with a water droplet. It is reported that water droplet in the Cassie-Baxter state is more mobile than in the Wenzel state. Since the surface morphology of the solid is rough, and the water droplet is in intimate contact with the solid asperities, called Wenzel state. When the water droplet rests on the tops of the asperities, this state is called Cassie-Baxter state. Figure 2-4 shows a droplet resting on a solid surface and its Wenzel and Cassie-Baxter states [6,7].

Figure 2-4 : Drawings of the water droplet on a solid surface (left), and its Wenzel and Cassie-Baxter states.

3. EXPERIMENTAL

3.1 Materials:

Polyvinyl chloride (PVC), polystyrene (PS), dimethylformamide (DMF) and dimethylacetamide (DMAC) were purchased from Sigma Aldrich. Nano graphene with a thickness of less than 10 nm was purchased from Angstron Materials. TiO_2 nanoparticles (powders) were fabricated by sol gel process in-house. These products were directly used in the electrospinning process without further purification. Organoalkoxysilane was purchased from Momentive Performance Materials.

3.2 Polyvinyl Chloride

Polyvinyl Chloride ($[-CH_2 = CH - Cl]_n$) (PVC) is a member of a family of polymers referred to as vinyls [71]. Around 100 years ago there was the first definite report of the polymerization of vinyl chloride. When vinyl chloride was first reported it was described as a white solid that could be heated to 130°C without degradation, however right after 130°C it becomes a black brown substance where the evolution of copious acid vapors occurs.

The first important breakthrough in the development of PVC was around 1930. Around 1930 several workers discovered that PVC could be plasticized by esters such as dibutyl phthalate. Early development of PVC was in Germany. Therefore, PVC was first produced on a full scale commercial basis in Germany in 1937. After discovery of PVC, continuous development has been observed in its formulation, particularly in the development of effective lubricants, stabilizers, processing aids and processing machinery properly designed to the needs of PVC [72].

Properties of PVC are below:

1. Low cost

2. The ability to be compounded to a wide range of flexible and rigid forms, including foams and coatings.

3. Good physical, chemical, and weathering properties.

4. Utility in a broad range of large volume applications.

5. Processability by a wide variety of techniques, solution and latex coating and impregnation.

PVC is almost everywhere in today's society such as uses in garden hoses, shower curtains, electrical insulation, auto and furniture upholstery, wall and floor coverings, dolls, toys, bottles, pipe, window and sliding frames, rain gutters and downspouts [71]. PVC is shown figure 3-1.

Figure 3-1: Polyvinyl Chloride (PVC)

3.3 Polystyrene

Polystyrene (PS) was named for a family of plastics derived of styrene monomer. Over 100 years ago styrene polymers were recognized in a laboratory setting. The discovery of styrene monomer was in the 1800's by Simon a German apothecary. The linear formula for polystyrene is $[CH_2CH(C_6H_5)]_n$. Polystyrene is softened by heat and when cooled down it hardens like other thermoplastics. General good properties of polystyrene are below:

1. Light in weight.
2. Easy to mold. In high speed injection machine polystyrene can be molded.
3. Tasteless; nontoxic and odorless.
4. Very good electrical properties.
5. Resistant to water as well as many chemicals; especially corrosive; inorganic liquids like acids or bases.
6. Good optical properties.

Melt index for PS is 200°C; average Mw (molecular weight) of PS is 192000 and softening point is 107°C. The physical properties of PS are dependent on its average Mw. Polymer has a low softening temperature in low molecular weight. Polystyrene is used to fabricate a great number of products due to low material cost; good physical properties and easy processability using several different methods such as injection molding, extrusion and sheet forming. Polystyrene is used in appliances, electronics, building, packaging and housewares like washers and dryers, tape recorders, signs, disposable cups and toys [73].

PS granules are shown in Figure 3-2.

Figure 3-2: Polystyrene (PS) granules in a plastic cup

3.4 Surfactant

Materials exhibiting the characteristic of modifying interfacial interactions by way of enhanced adsorption at interfaces are generally referred to as surface active agents or surfactants. Surfactant are used in applications such as motor oils and other lubricants, personal care products, laundry detergents specialized pharmaceutical formulations and food additives. Surfactants possesses a characteristic chemical structure that consists of molecular components that will have little attraction for the solvent or bulk material, called a hydrophobic group and chemical units that will have a strong attraction for the solvent or bulk phase, called hydrophilic group [74].

The hydrophilic (or head) group will be ionic or highly polar, so that it can act as a solubilizing functionality. In a nonpolar solvent such as hexane the same groups will function in the opposite sense [74]. The hydrophobic group is generally a long-chain hydrocarbon radical, although there are examples using halogenated or oxygenated hydrocarbon or siloxane chains. The most useful chemical classification of surfactant is primarily based upon the nature of the hydrophile, with subgroups being based upon the nature of hydrophobe. There are four general groups of surfactants which are defined as follows [74]:

1. Anionic: the hydrophilic group carrying a negative charge.
2. Cationic: the hydrophile bearing a positive charge.
3. Nonionic: the hydrophile has no charge, however derives its water solubility from polar groups.
4. Amphoteric (and Zwitterionic), in which the molecule contains or can potentially contain, both a negative and a positive charge [74].

3.5 AFM Characterization

Atomic force microscopy (AFM) is an emerging tool for nanocharacterization and has wide spread application owing to its capability to operate in various modes for getting different information. AFM modes include lateral force microscopy, force modulation microscopy, electrostatic force microscopy. In AFM, a cantilever is vibrated across the sample surface that detects the sample topography, which is converted into an image with help of a laser on the tip and a photosensitive position detector unit. AFM is employed to distinguish the size of the particle shown in Figure 3-3.

Figure 3-3 : TiO_2 cluster **particle size of 59nm measured by AFM**

3.6 Method

PS and PVC were separately dissolved in solvents (dimethylformamide and dimethylacetamide) at a ratio of 0.8:0.2 prior to the electrospinning process. Electrospinning experiments were conducted at various pump speeds, DC voltages and spinning distances. Nanosize graphene (thickness less than 10 nm with a diameter of 600 nm) and TiO_2 nanoparticles (10-25 nm) were added into polymeric solutions at varying percentages. Fiber size and morphologies were analyzed using scanning electron microscopy (SEM) as shown in Figure 3-4 to 3-14. Figure 3-15 shows the electrospinning of polymeric solutions and resultant nanofibers on the grounded collector. Electrospun PVC and PS fibers with different diameters were used in the contact angle measurements. CAM 100 contact angle goniometer was used to determine the water contact angle of the fiber films as shown in Figure 3-16. Thin films of electrospun fibers were placed on a glass plate, and a single drop of DI water was transferred on top of the films by a syringe. At least, five static contact angle measurements were read and the results were averaged for each sample. TiO_2 nanoparticles were fabricated using a sol-gel process. Following chemicals were utalized to prepare TiO_2 nanoparticles (or nano powders): Isopropanol and Titanium (IV) Butoxide were mixed for about 10 minutes, and then 10% HCl solution was added drop wise using a pipet. As the gel forms, it was dried at 150°C for 24 hours (or until completely solidified). After the mortar grinder step or pulverizing, the amorphous TiO_2 nanoparticles were annealed at 550°C for 2 hours.

Figure 3-4 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), d=25cm, v=25kv m=2.5ml/hr).

Figure 3-5 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), d=15cm, v=15kv m=4ml/hr).

Figure 3-6 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 0.5%Graphene d=30cm, v=25kv m=1.5ml/hr).

Figure 3-7 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 1%Graphene d=30cm, v=25kv m=1.5ml/hr).

Figure 3-8 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 1% TiO_2 d=25cm, v=25kv m=1ml/hr).

Figure 3-9 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 2% TiO_2 d=25cm, v=25kv m=1ml/hr).

Figure 3-10 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 4% TiO_2 d=30cm, v=25kv m=1ml/hr).

Figure 3-11 : SEM images of PS fibers with processing parameters (PS&DMF (80:20), 8% TiO_2 d=30cm, v=25kv m=2.5ml/hr).

Figure 3-12 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 2% TiO_2 d=30cm, v=25kv m=1.5ml/hr).

Figure 3-13 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 4% TiO_2 d=30cm, v=25kv m=1.5ml/hr).

Figure 3-14 : SEM images of PVC fibers with processing parameters (PVC&DMAC (80:20), 8% TiO_2 d=30cm, v=25kv m=2.5ml/hr).

Figure 3-15 : Photograph showing the electrospun nanofibers on the grounded collector.

Figure 3-16: Contac angle measurement goniometer set up (CAM 100**).**

4. RESULTS AND DISCUSSION

4.1 Superhydrophobic Behavior of Electrospun Micro and Nanofibers

Figure 4-1 shows the SEM images of PVC and PS electrospun fibers that were obtained at 2.5 ml/hr pump speed, 25 kV DC voltage and 25 cm spinning distance. As can be seen, fibers diameters of PVC are between 200 and 500 nm, while that of and PS are between 400 nm and 1.25 µm. We also determined that the distributions of PVC fibers are more uniform than that of PS fibers, which may be because of the different viscosity and molecular structures of the polymers. Additionally, changing in the electrospinning conditions resulted in different fiber size and shape.

Figure 4-1 : SEM images of PVC (left) and PS electrospun fibers obtained at 2.5 ml/hr pump speed, 25 kV DC voltage and 25 cm spinning distance.

Superhydrophobic properties of the polymeric fibers should improve significantly by changing the roughness, voids, fiber size and shape and surface hydrophobicity of the polymers [2, 13]. In our study, we determined that the water contact angles are usually higher as the fiber diameters become in smaller sizes. Figure 4-2 shows the water contact angle values of PVC and

PS fibers, respectively. Although the fiber diameter of PVC is smaller than that of PS, the water contact angle value (165°) of PS fibers (0.800 – 1.29 µm) is higher than that (152°) of PVC fibers (0,2-0,5 µm). This may be attributed to the molecular structure, initial hydrophobicity and surface roughness of PS fibers. Figure 4-2 shows the water contact angle values of PVC and PS electrospun fibers. Table 4-1 also gives the contact angle values of various size polymeric fiber films.

Figure 4-2 : Water contact angle values of PVC (above) and PS fibers obtained at 2.5 ml/hr pump speed, 25 kV DC voltage and 25 cm spinning distance.

Table 4-1 : Contact angle values of various size PS and PVC fiber films.

Polymer Types	**Fiber Diameter (µm)**	**Contact Angle (°)**
Polystyrene	0.800 – 1.29	164.55
	1.90 – 2.40	123.69
	4.81 - 7.60	127.02
Polyvinylchloride	0.200 -0.500	152.00
	0.230-0.280	142.00
	0.870-1.03	138.17

4.2 Superhydrophobic Behavior of Electrospun PVC Nanofibers with Graphene Inclusion

In this research, nanosize graphene flakes were added into PVC polymeric solution at different weight percentages (0.5, 1, 2, 4%), and then electrospun at 30 cm distance, 25 kV DC voltage and 1.5 ml/h pump speed to determine the amount of graphene on the water contact angle (superhydrophobicity). The reason for adding graphene particles in the polymer are to increase the surface roughness, voids and hydrophobicity of the electrospun fibers, which may directly affect the superhydrophobicity. Figure 4-3 shows the contact angle values of graphene added nanocomposite fibers. The water contact angles of the test results are also given in Table 4-2.

Figure 4-3 : Water contact angle values of PVC fibers (PVC&DMAC 80:20), 0.5%Graphene (d=30cm, v=25kv, m=1.5ml/hr)obtained a, 1%Graphene b, 2%Graphene c, 4%Graphene d.

Table 4-2: Contact angle values of various size nano graphene into PVC fiber films.

Polymer Types	**Graphene Percentage %**	**Contact Angle (°)**
Polyvinylchloride	**0.5**	**141.81**
	1	**151.53**
	2	**165.29**
	4	**166.26**

As is seen from Figure 4-3 and Table 4-2, increasing graphene concentration into the electrospun fibers gradually increases the water contact angle values. In the absence of graphene, water contact angle of the fibers is below 140°; however, the water contact angle values of 0.5, 1, 2 and 4% graphene added nanocomposite fibers are 141.8, 151.5, 165.3 and 166.3°, respectively. This indicates that graphene inclusions in the polymeric fibers drastically change the surface morphology and chemistry, which results in higher contact angles and the superhydrophobic surfaces. Note that graphene concentration higher than 4% affected the electrospinability of the polymeric solutions.

4.3 Superhydrophobic Behavior of Electrospun PS and PVC Fibers with TiO2 Nanoparticles

In the present study, sol-gel driven TiO_2 nanoparticles (10-25 nm) were added into PVC and PS polymeric solutions at different weight percentages (1, 2, 4, 8), and then electrospun at 25 cm distance, 25 kV DC voltage and 1 ml/h pump speed to determine the effects of TiO_2 nanoparticles on the contact angle values of nanocomposite fibers. Figures 4-4 and 4-5 show the water contact angle values of PVC and PS nanocomposite fibers. Table 4-3 also gives the water contact angle values of the same PVC and PS nanocomposite fibers.

Figure 4-4 : Water contact angle values of PS nanocomposite fibers (PS&DMF 80:20), 1% TiO_2 (d=25cm, v=25kv, m=1ml/hr)obtained a, 2% TiO_2 b, 4% TiO_2 c, 8% TiO_2 d.

Figure 4-5 : Water contact angle values of PVC nanocomposite fibers (PVC&DMAC 80:20), 1% TiO_2 (d=25cm, v=25kv, m=1ml/hr) obtained a, 2% TiO_2 b, 4% TiO_2 c, 8% TiO_2 d.

As can been seen from Table 4-3, the PS nanocomposite fibers obtained at 1, 2, 4 and 8% TiO2 nanoparticles give 155.5, 156.1, 164.5 and 177.5° water contact angle values, respectively, while the PVC nanocomposite fibers with the same concentrations and spinning conditions give 151.3., 164.3, 168.3 and 165.0°. The highest contact angle value (177.5°) was received from the PS nanocomposite fiber obtained at 8% TiO2 nanoparticles. Additionally, increasing TiO2 nanoparticles in both polymers result in higher contact angle values. TiO2 is a hydrophilic material (θ below 5°) [82], and we assume that the most of the TiO2 nanoparticles were

embedded into polymeric solution. Thus, there is no direct interaction between the water molecules and TiO2 nanoparticles to reduce the contact angle values.

Initially, it was expected that the graphene added nanocomposite fibers might offer higher superhydrophobicity than TiO2 nanoparticles since graphene has much higher water contact angle value (θ over 80°). However, the results show that TiO2 nanocomposite fibers have higher contact angle values, which may be because of the nanoscale gaps/bumps/voids formed on the fiber in the presence of TiO2 nanoparticles. A further study needs to be conducted to clarify the situation.

Table 4-3 : Contact angle values of various size TiO_2 nanoparticles into PS and PVC fiber films.

Polymer Types	TiO_2 **Nanoparticles %**	**Contact Angle** (°)
Polystyrene	**1**	**155.50**
	2	**156.08**
	4	**164.53**
	8	**177.48**
Polyvinylchloride	**1**	**151.28**
	2	**164.32**
	4	**168.32**
	8	**164.98**

4.4 Heat Treatment Effects on Superhydrophobici Behavior of Electrospun Fibers

In this part of the work, we studied the effects of heat treatment on the contact angle values of electrospun PVC and PS fibers at 60, 80, 100 and 120ºC in the presence and absence of nanoscale inclusions. Figures 4-6 to 4-10 show the effect of the heat treatment effects on the contact angle values for various PS samples produced using different DMF solvents. Higher concentration typically produces larger diameters of fibers, which result in lower contact angle values on the fiber films. Table 4-4 gives the water contact angle value of PS fibers obtained at varying temperatures.

Figure 4-6: Water contact angle values of PS fibers (PS&DMF (80:20), d=20cm, v=20kv m=3ml/hr)obtained at 60 ºC a, 80 ºC b, 100 ºC c and 120 ºC d.

Figure 4-7: A Water contact angle value of PS fibers (PS&DMF (70:30), d=20cm, v=20kv m=3ml/hr) obtained at 60 ºC a, 80 ºC b, 100 ºC c and 120 ºC d

Figure 4-8: Water contact angle values of PS fiber (PS&DMF (60:40), d=20cm, v=25kv m=3ml/hr) obtained at 60ºC a, 80 ºC b, 100 ºC c and 120 ºC d.

Table 4-4 : Contact angle values of PS fibers obtained at varying temperatures.

Polymer Types	**Contact Angle Values at Different Temperatures**			
	60ºC	80ºC	100ºC	120ºC
PS&DMF (80:20)	156.95	158.09	155.38	101.03
PS&DMF (70:30)	132.07	138.59	150.07	121.57
PS&DMF (60:40)	145.92	146.27	157.39	130.84

At smaller fiber diameters obtained using PS&DMF at 80:20 solvent concentrations (Table 4-4), heat treatment effects on contact angle values are fairly low, and after 100° C, the contact angle value reduces from 155.4 to 101.0°. The same effects on larger fiber diameters are reasonably high. For instance, PS fiber obtained using PS&DMF (60:40) has a contact angle value of 157.4° at 100 °C heat treatment, and then reduce to 130.8° at 120° C.

High molecular weight polystyrene is a hard, glassy solid at room temperature. However, when it is over 100°C it becomes flexible. At higher temperatures it may became somewhat rubbery. Temperature at which it softens is known as the second-order or glass transition temperature, T_g. Below the transition temperature point polymer chains are rigid and segments of the chains cannot move. When the polymer goes above the T_g chain segment undergoes rotation; since the chains can slip past each other and when stress is applied, the material becomes more flexible [72]. Rotation occurs due to carbon-carbon bonds in the chain and they can be twisted easily. Two bonds can act as an axis of rotation permitting carbon atoms (and the groups attached to them) to rotate. Glass transition temperature (Tg) of polystyrene is around 100 °C [72], and exceeding the Tg can permanently change size, shape, porosity and surface

composition of the fibers, which result in lower contact angles on the surface of PS fibers. Additionally, Tg effects on smaller fibers are higher than the larger fibers. This may be related to the surface area, surface energy and Tg shift at nanoscale. A future studies will be need to identify this assumptions.

Figure 4-9 : Water contact angle values of PVC fibers (PVC&DMAC (80:20), d=25cm, v=25kv m=1ml/hr) obtained at 60 ºC a, 80 ºC b, 100 ºC c, and 120 ºC d.

Similar experimental results were seen on PVC fibers as is shown in Figures 4-9. The detailed experimental results of PVC fibers at different heat treatments were also given in Table 4-5. Glass transition temperature of PVC is around 82°C [70]. When the temperature of PVC is below *Tg*, it is in a brittle state. But, above T_g, it shows greater resilience, impact strength and

flexibility. Additionally, other physical and physicochemical properties of PVC fibers can drastically change above the Tg point, which in turn may affect the contact angle values of the PVC fibers.

Table 4-5 : Water contact angle values of PVC fibers obtained at various temperatures.

Polymer Types	**Contact Angle Values at Different Temperatures**			
	60ºC	**80ºC**	**100ºC**	**120ºC**
PVC&DMAC(80:20) m=1ml/hr	143.51	149.25	137.73	132.85
PVC&DMAC(80:20) m=2.5ml/hr	134.35	137.97	139.67	120.44
PVC&DMAC(80:20) m=4ml/hr	140.54	140.94	143.54	119.23
PVC&DMAC(85:15) m=2.5ml/hr	164.69	151.36	137.75	128.66

In order to determine the heat treatment effects on the contact angle values of the PVC nanocomposite fibers, a number of experiments were conducted at various temperatures. PVC nanocomposite fibers were produced using nanoscale graphene inclusions. Figure 4-10 shows the contact angle values of PVC nanocomposite fibers as a function of graphene and temperatures. The same results are also presented in Table 4-6. As is seen, the contact angle values of PVC nanocomposite fibers obtained using 0.5% graphene are 145.9, 151.2, 152.9 and 135.1° at 60, 80, 100 and 120° C, respectively. The contact angle values of PVC nanocomposite fibers obtained using 4% graphene are 158.1, 162.1, 149.4 and 138.5° at the same heat treatments. This indicates that the nanoscale graphenes in the PVC fibers considerably increase the contact angle vales of the PVC fibers by changing some physical and physicochemical properties.

Figure 4-10 : Water contact angle values of PVC nanocomposite fibers(PVC&DMAC (80:20), d=30cm, v=25kv m=1.5ml/hr) obtained at 60 ºC heat treatment and 0.5%Graphene a, 80 ºC and 1%Graphene b, 100ºC and 2% Graphene c, and 120ºC and 4%Graphene d.

Table 4-6: Water contact angle value of PVC nanocomposite fibers obtained at various temperatures.

Polymer Types	**Contact Angle Value In Different Temperature**			
	60ºC	**80ºC**	**100ºC**	**120ºC**
PVC&DMAC 0.5% Graphene	145.85	151.23	152.86	135.08
PVC&DMAC 1% Graphene	155.38	161.33	151.16	140.13
PVC&DMAC 2% Graphene	155.65	152.70	154.73	138.25
PVC&DMAC 4% Graphene	158.10	162.13	149.40	138.53

4.5 Superhydrohobic Behavior of Electrospun Fibers with Surfactant Treatment

In this study, surfactant solutions were prepared using Organoalkoxysilane with DI water at various weight percentage (0.25, 0.5, 1), and then the PVC nanocomposite fibers produced using graphenes were dipped into these solutions. Effects of surfactant surface treatment are shown in both Figures 4-11 and Table 4-7.

Figure 4-11 : Water contact angle values of PVC nanocomposite fibers (PVC&DMAC (80:20), solution d=30cm, v=25kv m=1.5ml/hr) obtained at 1% graphene into 0.25% Organoalkoxysilane a, 0.5% graphene into 0.5% surfactant solution b, 2% graphene into 1% surfactant solution c, and 4% graphene into 1% surfactant solution d.

Table 4-7 shows that the PVC nanocomposite fibers produced using 0.5% graphene gave 141.5, 148.0 and 155.3° contact angles values at 0.25, 0.5 and 1% surfactant concentrations, respectively. At higher graphene loadings, the contact angle values tend to decrease, which may be due to the orientation of the surfactant molecules, where hydrophobic graphene surface interact with the hydrophobic tails of the surfactant molecules rather than hydrophilic heads [70]. Thus, hydrophilic heads may reduce the contact angles values of the nanocomposite fibers at higher graphene concentrations.

Table 4-7 : Contact angle values of PVC nanocomposite fibers obtained at various weight percentages of surfactant solutions.

Polymer Types	**Contact Angle Value at Different Surfactant Concentrations (%)**		
	0.25%	**0.5%**	**1%**
PVC&DMAC with 0.5% Graphene	141.52	148.00	155.34
PVC&DMAC 1% Graphene	168.19	157.65	149.34
PVC&DMAC with 2% Graphene	161.20	164.78	158.47
PVC&DMAC with 4% Graphene	159.04	153.12	151.99

5. CONCLUSION

Micro and nanofibers of polystyrene and polyvinyl chloride were fabricated using electrospinning process at various spinning conditions. Also additives such as TiO_2 and nano graphene were added into polymeric solutions to produce micro and nanocomposite fibers. Water contact angle measurements were conducted on those electrospun fibers before and after the surface treatment and heat treatment. The measurements revealed that the contact angle values not only depended on the fiber diameter, but also on the chemical structures of the polymers and surface roughness of the fiber. The present data shows that these flexible and high surface area nanocomposite fibers can have a number of industrial applications in textile, military, electronics and biomedical engineering as self cleaning surface, non-wettable fabric, antibacterial surface, low friction devices, as well as MEMS, NEMS, microfluidics and nanofluidics parts.

REFERENCES

LIST OF REFERENCES

1. Gupta, P., Asmatulu, R., Wilkes, G. and Claus, R.O. "Superparamagnetic flexible substrates based on submicron electrospun Estane® fibers containing MnZnFe-Ni nanoparticles," *Journal of Applied Polymer Science*, 2006, Vol. 100, pp. 4935-4942.

2. Ramakrishna, S. "An Introduction to Electrospinning and Nanofibers," World Scientific, 2005.

3. Gogotsi, Y. "Nanomaterials Handbook," CRC Press, 2006.

4. Asmatulu, R., Khan, W., Nguyen, K.D., and Yildirim, M.B. "Synthesizing Magnetic Nanocomposite Fibers for Undergraduate Nanotechnology Education," (in press, *International Journal of Mechanical Engineering Education*).

5. http://nanotechweb.org/cws/article/lab/38728/1/image2, accessed June 7, 2009.

6. A.W. Adamson, A.P. Gast, "Physical Chemistry of Surfaces, sixth addition," John Wiley and Sons, USA, 1997.

7. http://en.wikipedia.org/wiki/Hydrophobic, accessed June 7, 2009.

8. Asmatulu, R. "Improving the dewetability characteristics of hydrophobic fine particles by air bubble entrapments," *Powder Technology*, 186 (2008) 184–188

9. Asmatulu, R. "Enhancement of Dewetability Characteristics of Fine Silica Particles," *Turk. J. Engin. Environ. Sci*., 26, (2002), pp. 513-520.

10. Zhai, L., Berg, M. C., Cebeci, F., Kim, Y., Milwid, J. M., Cohen, R. E. and Rubner, M. F. "Patterned Superhydrophobic Surface: Toward a Synthetic Mimic of the Namib Desert Beetle" *Nano Lett.* **2006**, 6, 1213.

11. Cebeci, F., Wu, Z., Zhai, L., Cohen, R. E. and Rubner, M. F. "Nanoporosity-Driven Superhydrophilicity: A Means to Create Multifunctional Antifogging Coatings," *Langmuir* **2006,** *22,* 2856-2862

12. http://www.gelwell.com/hydrophobic%20coating.jpg, accessed June 7, 2009.

13. http://www.che.ncsu.edu/dickeygroup/gallery1.htm, accessed June 7, 2009.

14. http://www.electrobright.com/magimplants7.jpg, accessed June 7, 2009.

15. HOW, T.V.US Patent, 4, 552, 707, 1985.

16. Woraphon Kataphinan.Ph.d dissertation, University of Akron, Akron, OH, 2004.

17. Kataphinan W. Thesis, University of Akron, Akron, OH 2001.

18. Rayleigh, J.W.S, Proc.R.Soc. London, 23,71,1879.

19. Taylor, G.I., Proc. R.Soc. London, A313, 453 (1969).

20. Taylor, G.I., Proc. R.Soc. London, A280, 383 (1964).

21. Taylor, G.I., Proc. R.Soc. London, A291, 159 (1966).

22. Formhals, A., US Patent, 1, 975,50,1934.

23. Berry, J.P., US Patent, 5, 024, 789, 1991.

24. Formhals, A., US Patent, 2, 349, 950, 1944.

25. Baumgarten, P.K. "Electrostatic spinning of acrylic micro fibers," J.of colloid and interface Science. Vol 36, PP.71-79. May 1971.

26. Doshi, J.N. Phd. Dissertation, University of Akron, Akron, OH, 1994.

27. Doshi, J.; Renekar, D.H.,J. Electrost. 1995, 35(2&3), 151-60.

28. Srinivasan, G. Phd. Dissertation, University of Akron, Akron, OH, 1994.

29. Srinivasan, G.; Renekar, D.H., Polym.Int. 1995, 36(2), 195-201.

30. Chun I.Phd. Dissertation, University of Akron, Akron, OH, 1997.

31. Fong, H.; Chun, I.; Renekar, D.H., Polymer 1999, 40(16), 4585.

32. Jaegar, R.; Bergshoef, M.M.; Martin, I.B., Christina; Schoenherr, H.; Vancso, G.J., Macromol. Symp. 1998, 127 (Rolduc polymer Meeting 10:"Petro" polymers vs "Green" Polymers, 1997, 14-150.

33. Jaegar, R; Schonherr, Vansco, G.J., Macromolecules, 196, 27, 7634-36.

34. Fong X. Phd. Dissertation, University of Akron, Akron, OH, 1999.

35. Fong X.; Renekar, D.H., Macromoi. Sci., phys. 1997, B36 (2), 169-173.

36. Kim J.Ph.d Dissertation, University of Akron, Akron. OH, 1997.

37. Kim, J.S.; Renekar, D.H., polymer.Eng.Sci.1999, 39(5), 849-854.

38. LNP Engineering Plastic, US Army soldier system, Advanced Material and processing, Citation 152, No.4, Oct 1997, P.4.

39. Stenoien et al., US Patent, 5, 840, 240, 1998.

40. Zarkoob, S.Ph.d Dissertation, University of Akron, Akron, OH, 1999.

41. Zarkoob, S.; Reneker, D.H.; Eby, R.K.; Husdon, S.D.;Ertley,D.;Adams, W., Polym. Prepr. (Am. Chem. Soc., Div.polym. chem.) 1998, 39(2), 244-245.

42. Huang, L., R.; Andrew McMillan, Robert P. Apkarian, Benham pourdeyhimi Vincent P. Conticelo, and Elliot L. Chaikof, Macromolecules 2000, 33, 2989-2997.

43. Fong H; Renekar D.H., in structure formation in polymer fibers; Electrospinning and Formation of Nano-fibers, Dr. Salem and M.V. Sussman, Eds 2001, 225-246.

44. Fong, H.; Chun, I.; Reneker, D.H., Polymer 1999, 40 (16), 4585.

45. Norris, I.D., Shaker, M.M., KO F.K., and MacDiarmid, A.G., Synth Met. 114,109 (2000).

46. Kim, J.S., Lee, D.S.Polym. J. (Tokyo) (2000), 32 (7), 616-618.

47. Bognitzki, M.; Frese, T.; Wendorff, J.H.; Grenier, A., Book of Abstract, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000, PMSE-173. Publisher: American Chemical Society, Wasington, D.C.

48. Bognitzki, M.; Frese, T.; Wendorff, J.H.; Greiner, A Polym. Mater. Sci. Engg. 2000, 82, 115- 116.

49. Suthar, A.; Chase, G.Tec (2001), 726, 26-28.

50. Wessling B, "Dispersion as the link between basic research and commercial application of Conducting polymer (polyaniline)'', Synthetic Metals, 9, 1998, 143-154.

51. Kataphinan W, Dabney S, Reneker D.H, Smith D, Akron UO, Electrospun Skin masks and uses thereof. Patent WO0126610. University of Akron; 2001.

52. Gibson P, McManus A, Meel C et at "Electrospun fibers and apparatus thereof." Patent WO0127365. University of Akron; 2001.

53. Fang D, Hsiao B, and Chu B, "Multiple jet electrospinning of non-woven Nano-fiber articles", polymer preprints 2004, 44(2), 59.

54. http://www.che.vt.edu/Wilkes/electrospinning/electrspinning.html.

55. Zufan, R. "Electrospinning of Nanofibers," Final 2005 RET Report.

56. http://en.wikipedia.org/wiki/Electrospinning.

57. http://www.eduprograms.deas.harvard.edu/reu05_papers/Berdy_David.pdf.

58. Pinton, N.J., Johnson, A.T., Macdiarmid, A.G., Muller, C.H., Theofylaktos, N., Robinson, D.C. and Miranda, F.A. "Electrospun polyaniline/polyethylene oxide nanofiber field-effect transistor," Applied physics letters, 2003, vol. 83, pp. 4244-4246.

59. Srinivasan, G. and Reneker, D.H., "Structure and morphology of small diameter electrospun aramid fibers," Polymer International 1994; 36: 195-201.

60. www.neotherix.com/technology.php.

61. Darrell H.Renekar "Bending instability of electrically charged liquid jets of polymer Solutions in electrospinning"

62. Renekar, D.H.; Yarin, A.L.; Fong, H.; .Koombhongse, S.Journal of Applied Physic 2000, 87, 4531-4547.

63. Spivak, A.F.; Denis, Y.A"Applied Physic letters 1998, 73, 3067-3069.

64. Yarin, A.L.S.Koombhongse and D.H.Renekar "Taylor cone and jetting form liquid droplets in electrospinning of Nano-fibers," journal of applied physic 2001 90(9) p. 4836-4846.

65. Fridrikh S.V, J.H.YU "Controlling the fiber diameter during electrospinning," physic review letters 2003: P.064501"

66. Feng "The stretching of an electrified non-Newtonian jet"

67. Fong H, Chun I and Reneker D.H "Beaded nanofibers formed during Electrospinning" Polymer 40(1999)4585-4592.

68. Veli E. Kalayci, Prabir K. Patra "Fundamental Investigations on Electrospun Fibers"

69. Larry L. Hench and John K. West " The Sol-Gel Process", Chemical Reviews, 1990, vol.90,33-72.

70. A.C Zettlemoyer " Hydrophobic Surfaces," Elsevier, 1968

71. Harold A. Sarvetnick "Polyvinyl Chloride," Van Nostrand Reinhold, 1969.

72. J.H.L. Henson and A. Whelan "Developments in PVC Technology," John Wiley and Sons, New York, 1973.

73. William C. Teach and George C. Kiessling “Polystyrene,” Reinhold, 1960.

74. Drew Myers “Surfactant Science and Technology,” VCH, 1988.

75. Asmatulu, R., Khan, W., Nguyen, K.D., and Yildirim, M.B. “Synthesizing Magnetic Nanocomposite Fibers for Undergraduate Nanotechnology Education,” *International Journal of Mechanical Engineering Education* (in press).

76. Asmatulu, R., Khan, W. and Yildirim, M.B. “Acoustical Properties of Electrospun nanopfibers for Aircraft Interior Noise Reduction,” ASME International Mechanical Engineering Congress and Exposition, Lake Buena Vista, Florida - November 13-19, 2009, pp. 1-7.

77. Khan, W., Asmatulu, R., El-Tabey, M.M., Ho, J. and Hamdeh, H.H. “Electrical Properties of Nanocomposite Fibers under Various Loads and Temperatures,” ASME International Mechanical Engineering Congress and Exposition, Lake Buena Vista, Florida - November 13-19, 2009, pp. 1-8.

78. Asmatulu, R., Davluri, S. and Khan, W. “Fabrications of CNT based Nanocomposite Fibers from the Recycled Plastics,” ASME International Mechanical Engineering Congress and Exposition, Lake Buena Vista, Florida - November 13-19, 2009, pp. 1-6.

79. Ceylan, M., Asmatulu, R., Khan, W. and Nuraje, N. “Superhydrophobic Behavior of Electrospun Micro and Nanofibers,” SAMPE Fall Technical Conference, Wichita, October 19-22, 2009, pp. 1-8.

80. Asmatulu, R., Dandin, V. and Khan, W. “Properties of Recycled PVC and PS Nanocomposite Fibers at Various NiZn Ferrite Loadings,” SAMPE Fall Technical Conference, Wichita, October 19-22, 2009, pp. 1-10.

81. Asmatulu, R., Khan, W., and Yildirim, M.B. “CNT Reinforced Nanocomposite Fiber Fabrication for Undergraduate Students,” 2008 ASEE Midwest Regional Conference, September 18-19, 2008, Tulsa, OK, pp. 1-7.

82. Stevens, C. I. Priest, R. Sedev, and J. Ralston “Wettability of Photoresponsive Titanium Dioxide Surfaces,” *Langmuir*, **2003**, *19* (8), pp 3272–3275.