Fabrication of Polyurethane/ Nanosilica Nanofibrous mats for Waterproof Breathable Fabrics and Assessing the Performance Characteristics

A Major Project Dissertation

submitted in partial fulfillment of the requirement for degree Of

Master of Technology *In* **Polymer Technology**

Submitted by

ARCHANA GANGWAR (2K15/PTE/11)

Under the Supervision of

Dr. ROLI PURWAR

DEPARTMENT OF APPLIED CHEMISTRY

DELHI TECHNOLOGICAL UNIVERSITY

DELHI-110042

DECLARATION

This is certified that the work presented in this thesis entitled **"Fabrication of Polyurethane / Nanosilica Nanofibrous Mats for Waterproof Breathable Fabrics and Assessing the Performance Characteristics"** is original and has been carried out by me for the degree of **Master of Technology** under the supervision of Dr. Roli Purwar, Assistant Professor, Department of Applied Chemistry, Delhi Technological University. This thesis is a contribution of my original research work. Wherever research contributions of others are involved, every effort has been made to clearly indicate the same. To the best of my knowledge, this research work has not been submitted in part or full for the award of any degree or diploma of Delhi Technological University or any other University Institutions.

Archana Gangwar

(Candidate)

CERTIFICATE

This is to certify that the M.Tech thesis entitled **“Fabrication of Polyurethane / Nanosilica Nanofibrous Mats for Waterproof Breathable Fabrics and Assessing the Performance Characteristics”** submitted to Delhi Technological University, Delhi-110042, in fulfillment of the requirement for the award of the degree **Master of Technology** by the candidate **Archana Gangwar** under the supervision of **Dr. Roli Purwar, Assistant Professor,** Department of Applied Chemistry. It is further certified that the work embodied in this thesis has neither partially nor fully submitted to any other university or institution for the award of any degree or diploma.

(Dr. Roli Purwar)

Supervisor

Department of Applied Chemistry

Delhi Technological University

(Dr. Archana Rani)

Head of the Department

Department of Applied Chemistry

Delhi Technological University

Delhi

ACKNOWLEDGEMENTS

Firstly, it gives me a great sense of pleasure to present the M. Tech. Final thesis undertaken during M. Tech. Final Year. I am grateful to my project guide **Dr. Roli Purwar** for her expert guidance, meticulous efforts, constructive criticism, inspiring encouragement, unflinching supports and invaluable cooperation which enabled me to enrich my knowledge and reproduce in the present form. Her continuous inspiration has helped me to complete this project.

I would also like to thank **Dr. Archana Rani**, Head of the Department, for giving his kind support, sharing of valuable knowledge and approval of necessary infrastructure.

I would also like to thank the faculty members Dr. Deenan Santhiya and Dr. Jay Singh for giving their support and approval of necessary infrastructure. They have also been helpful in providing valuable insights throughout this project. I would also like to acknowledge Mr. Sandeep from the Department of Applied Physics, Delhi Technological University, for enabling us to perform experiments using his infrastructure and equipment.

I would also like to thank the laboratory staff of the department for extending their kind support and sharing their valuable time for the completion of this project.

I also thank my seniors, friends and colleagues whose inspiration and motivation helped in the completion of this project.

Archana Gangwar

(2K15/PTE/11)

ABSTRACT

Polyurethane nanofibres were prepared by electrospinning technique using the solvent dimethylformamide. In this study the solution properties (viscosity and molecular weight) of Polyurethane and electrospinning process parameters were determined. Brookfield Viscometer and Ubbelohde capillary Viscometer is used to measure the viscosity of solution and molecular weight of polymer respectively. The results show that the viscosity of the polymer increases with increase in concentration of solution linearly. Solution viscosity increases with respect to time and decreases with respect to temperature. Molecular weight of Polyurethane is [M] = 6,231. This is in the range of fiber forming polymer.

Electrospinning process parameters like concentration of solution, voltage and distance of electrospun nanofiber diameter have been investigated for Polyurethane nanofibrous mats. Fiber diameter and contact angle of water were investigated for development of waterproof breathable nanofibrous mat. After optimization of parameters Polyurethane / nanosilica based nanofibrous mats and two & three layered waterproof breathable fabrics were prepared and assessing the performance characteristics by using contact angle, water vapor transmission rate, air permeability and water wicking test methods. Morphology of the electrospun nanofibres was examined by the software image J, Contact angle test, water vapour transmission rate, air permeability and water wicking test was conducted to check the waterproofness and breathability of waterproof breathable fabrics. The nanofibre diameter increase with increase in concentration and voltage, but decrease with an increase in distance. And the contact angle of nanofibrous webs increases with decrease in diameter. The contact angle varies from 79±3° to 118±2° for

various Polyurethane nanofibrous mats. Polyurethane / nanosilica nanofibers were successfully obtained with maximum contact angle 138±1°. In waterproof breathable fabrics, polyester fabric has high waterproofness and breathability than cotton. Silica nanoparticles improve the waterproofness and breathability both in two layer, PU + nanosilica deposited cotton (CS) fabric and three layer, PU + nanosilica deposited on cotton + polyester (CPS) fabric. Polyurethane nanofibrous cotton (CU) fabric has lower waterproofness and breathability.

TABLE OF CONTENTS

Content **Page**

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

Waterproof, breathable fabrics are produced to be used in different garments [1]. These fabrics are engineered with the aim of protecting the wearer from weather conditions like wind, snow, and rain, as well as preventing excessive loss of body heat [1, 2]. The breathability of the fabric is the quality of clothing to allow the transmission of moisture vapor by diffusion and therefore facilitate evaporative cooling [3-5]. Thus breathability is an important factor of clothing comfort. It is the top attribute of apparel from the consumer's point of view [1]. Such abilities have opened a wide range of applications for these types of fabrics in many fields such as the apparel industry (sportswear, leisure and outdoor clothing), high performance filtration, harmful chemical area, orthopedic dressing and protective high-tech clothing (firemen, military, medical, personnel, postmen) [1-9].

Electrospinning is a fiber forming technique. Nanometer to micron range of fibers can be produced in the electrospinning process by electrostatic force. Non-woven mats of electrospun nanofibers provide exceptionally high ratios of surface area to volume with very small pores that prevents from penetration of water droplets while it is large enough to allow easy water vapor transfer from the body to the environment [1, 10].

Polyurethane is a widely used elastomer in coatings, adhesives, binders, air filters, protective textiles, sensors, and in biomedical fields viz. biomedical device, tissue engineering, wound dressing materials, antimicrobial filters, and many more [11-13].

Polyurethane (PU) electrospun mats are very promising in tissue engineering [12–14], protective clothes [7, 17], biosensor [18], nanofiltration [19], smart textiles, nanocomposites and may more

[10, 11, 20]. Asghar sadighzadeh et al. [5] showed that an improvement of waterproof, breathable properties using varying parameters (concentration of polymer and voltage) and find PU fiber web is better than PAN and PES. Some researchers have focused on production of polyurethane nanofibres from using different solvents and show the influence of solvents properties on morphology [11] and mechanical properties of polyurethane electrospun fibre mats [21]. Gorji et al. [17] showed that PU electrospun mat as good windproof membrane with acceptable water vapor transfer ability and low air permeability. In researches reported by Ahn et al. and Yoon et al. [22, 6] the electrospun PU nanofibrous membrane showed better water vapor permeability than the PTFE membrane and higher water resistance than nylon and polyester waterproof fabrics. However, it was still of lower air permeability rate, which affects the cloth comfort [1].

Silica is an attractive material for fabric coatings because it is characterized by its nontoxicity, biocompatibility, chemical inertness, thermal stability, controllable pores, and tunable surface, harmless and inexpensive [22-35]. Mesoporous silica materials have high surface area, large pore volume, and tunable pore structure and well defined surface property for modification [36-38]. The textiles modified by coating consisting of silica nanoparticles and organic silane showed excellent water repellent property and self cleaning behavior [39, 40]. The nano-sized silica acts as reinforcing agent to improve the hardness, strength [41], and thermal stability [42] of the polymers [43]. Mesoporous silica nanoparticles are used in drug delivery [44-46], biomedical applications and in tissue regeneration [48]. Silica nanoparticles are currently manufactured as additives for a film forming agent, fecade coating, and biological medicine [49-51].

Yi Chen et al. reported that the modification of PU leather coatings with Nanosilica, to improve the breathability or wear comfort of PU leather [52]. Xue et al. reported the complex coating of amino and epoxy functionalized silica nanoparticles with epoxy-functionalized cotton textiles generate a dual-size surface roughness and super hydrophobic surfaces [53]. Qinwen Gao et. al have reported the use of silica sol and hexadecyltrimethoxysilane (HDTMS) to impart extremely high hydrophobicity to both cotton and polyester fabrics [54]. Bae et al. prepared superhydrophobic cotton fabrics by the combination of the silica nanoparticles and a cost-effective water-repellent agent [55, 56]. Xu et al. fabricated the superhydrophobic surface on cotton fabrics by combining the surface roughness created by silica nanoparticles and zinc oxide nanorods and low surface energy modified by DTMS [55, 57].

Research problem and goal

The desired waterproofness and breathability both cannot be maintained in conventional barrier fabrics simultaneously. Low pore size of materials has good barrier properties that can allow direct passage of air through membranes and carries moisture in the form of vapours. PU nanofibres and nanosilica can improve the breathability and waterproofness simultaneously because they can create nanoroughness on the fabric surface. So far in the literature search, silica nanoparticles are applied to the textile substrates as finishing agent to improve the hydrophobicity of the fabric. The application of silica nanoparticle, in the preparation of polyurethane nanofibrous mats has not been reported in the literature. This may be the potential solution for the desired waterproofness and breathability. Therefore the objective of this work was to prepare PU/ nanosilica nanofibrous mat and develop the waterproof breathable fabrics.

The following specific objectives emerge from the goal of this study;

1. To check the solution properties viscosity and molecular weight by Brookfield Viscometer and Ubbelohde Capillary Viscometer.

2. Optimize the electrospinning parameters of PU nanofibers without beads or curls on which maximum contact angle is obtained.
3. Optimize the parameters on which PU nanosilica based nanofibers are obtained with maximum contact angle.
4. Examine morphology, diameter of nanofiber and waterproof ability using Scanning electron microscope, software image J and Contact angle test respectively.
5. Fabrication of waterproof breathable fabrics and assessing the performance characteristics by using Contact angle test, Water vapor transmission rate, Air permeability test and Water wicking test.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Clothing forms an essential part of the human's ancient times. It has been approximated that humans began wearing clothes at least 83,000 years ago and maybe as early as 170,000 years ago [2]. It became compulsory for humans to cover their body for preservation of the environment as they began moving long distances in cold weather [2]. Hence, since the starting, one of the basic functions of clothing is the preservation of distinct elements. Protective clothing is used today for different purposes like flame, heat and cold. They can protect the wearer from chemical, mechanical, electrical, biological, and radiation [4].

Comfort can be defined as "A state of physical relaxation and freedom from discomfort". Clothing comfort is classified into three main categories: tactile, thermal, and aesthetic comfort [6]. However, it can also be classified as mechanical and thermal comfort. Thermal comfort can be determined by the air permeability and water vapor permeability of fabric. Mechanical comfort can be evaluated by its rigidity, tensile properties, improved hand and smoothness [2]. Breathability of the fabrics plays a key role in comfort properties of clothing.

Breathability and waterproofness are two different abilities. Breathability of fabrics permit the transfer of air and water vapor from the one side of fabric to another, while waterproof property restricts the transmission of water drops from outside the fabric to inside and protect the wearer from getting wet. Therefore, it is a challenge to design fabrics that permit the transfer of water vapor, air, and perspiration from the inside of the fabric to the outside and simultaneously restrict the water droplets from the outside to the inside [7].

These fabrics have the capability to prevent liquid penetration and can resist loss of body heat while still maintaining comfort by granting water vapor transfer through the clothing. The calmness between different features can be changed based on end use. Such abilities have opened a wide range of utilizations for these types of fabrics in various fields such as the apparel industry (sportswear, leisure and outdoor clothing), high performance filtration, harmful chemical area, orthopedic dressing and protective, high-tech clothing such as firemen, military, medical, personnel, postmen [1]. Waterproof- breathable fabrics can be classified into various types based on the method of their fabrication.

2.2 Methods of Developing Waterproof Breathable Fabrics

In the market, waterproof breathable fabrics are introduced as raincoats. These types of fabrics have an outer layer coated with crude rubber called face fabric [9]. Now a day a lot of improvements are done on waterproof fabrics. Comfort is one of the latest changes that come through breathability. This type of fabric can easily absorb the perspiration vapors and provide the wearer a sense of flexibility. The following categories of waterproof breathable fabrics are discussed below according to handbook of technical textiles.

(1) Tightly woven:

Tightly woven synthetic microfilament

Tightly woven cotton

(2) Membranes:

Microporous membrane

Hydrophilic membrane

(3) Coatings:

Hydrophilic coating

a. Tightly woven fabrics

The fabrics woven by oxford weave come in the category of tightly woven fabrics. This is the first kind of waterproof breathable fabric known as “Ventile”. Long staple, plied and combed cotton yarns and synthetic microfilaments are used to woven the fabric [4]. Such yarns have high density and the fabric have minimum pores. Very high pressure of air and water is required to penetrate such kind of fabric. Cotton fibres swell when the fabric is dipped into water and the pore size reduces further after wetting. But synthetic filaments do not swell after wetting [2]. Synthetic microfilament yarns show better water repellent properties than cotton. To obtain the desired results these fabrics are coated further.

b. Microporous membranes and coatings

Diameter of pores nanometers to 01 microns is possible in microporous membranes and coatings [2]. Nanometer diameter of pores, creates nanolevel of surface roughness. That’s why hydrophobicity comes to these types of membranes and coatings. PTFE (Polytetrafluoroethylene) membranes, the trade name Gortex® is one of the examples of microporous membranes or coatings (Brzeziński et al 2005). PTFE membranes when applied onto the fabric, it generates about 1.4 billion tiny holes per cm2 of the fabric. These holes are much larger than water molecules, but smaller than tiny rain drops [4]. Various methods are available by developing these membranes and coatings. (Midha & Mukhopadhyay, 2008):

Solvent extraction

Wet coagulation

Melt blown technology

Bonding of point technology

Radio frequency beam radiation

c. Solid membranes and coatings

In solid membranes and coatings, no pores or holes are available. They are the thin hydrophilic films consist of modified polymers. They diffuse moisture by adsorption diffusion desorption or by molecular diffusion process [9]. To obtain better properties hydrophilic and hydrophobic components can be combined for the development of solid membranes and coatings [2]. A combination of hydrophobic and hydrophilic urethane components can develop hydrophilic membranes and coatings, according to researchers. While obtaining and maintaining the physical properties and improving the other properties [4].

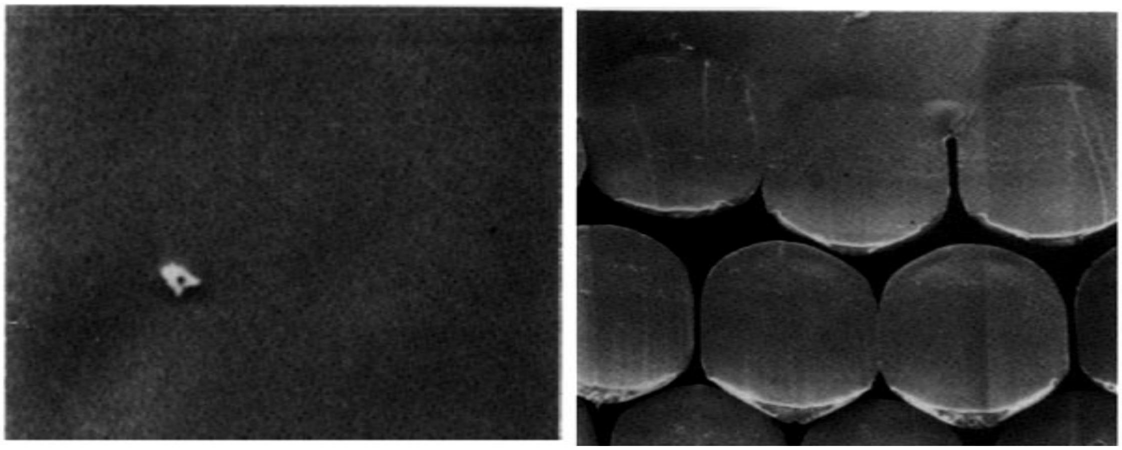


Figure 1 Left: Image of surface of coated hydrophilic fabric created by Shirley Institute.

Right: Fabric cross sectional structure [2].

For developing waterproof breathable fabrics, solid membranes and coatings is one of the methods. Other methods like microporous membranes and hydrophilic coatings. In case of membranes, a hydrophilic material like polyurethane is permeated with microporous material. And in case of coatings, hydrophilic polymer coatings are applied over microporous film. And that has been attached to the fabric. These types of coatings enhanced waterproofing capacity. But breathability does not decrease to a large extent [4].

2.3 Nanofiber membrane for protective textiles

Protective textiles protect the wearer from harmful substances such as water, heat and chemicals. That's why they gaining the lower permeability and higher repellency. To attain higher protective properties against harmful materials, protective textiles influences lower breathability (Bagherzadeh et al., 2012). A protective layer made with nanofiber mats may improve aerosol protection without powerful decrease of water vapor transmission (Schreuder-Gibson et al.). Gibson et al. mentioned that the other importance of directly depositing nanofiber mats on apprel is, they can solve the seam sealing problems, thus manufacturing cost reduces. Bagherzadeh et al., (2012) compared comfort properties of fabrics such as Gortex® among other fabrics. Other fabrics like a control group of exact woven fabric substrate without nanofibrous mats and multilayered electrospun nanofiber mats equipped fabric (MENMEF). Multilayered electrospun nanofiber mats equipped fabric is prepared by optimizing electrospinning parameters of polyacrylonitrile dissolve in dimethylformamide (DMF). Electrospinning parameters like concentration of solution, distance, voltage and electrospinning time. Air permeability, water repellency and water vapor transmission were measured. And it was found that increasing electrospinning time and the concentration of the polymer solution could result in lower air permeability, higher waterproofness and slight changes of breathability for multilayered electrospun nanofiber mats equipped fabric. It was concluded that PTFE coated Gortex fabric compared with multilayered fabrics with nanofiber membranes exhibit lower water vapor transmission, lower windproof properties but higher water repellency (Bagherzadeh et al., 2012). Varying electrospinning duration (density of the web) and polymer concentration, different applications could be achieved. Gorji et al. 2012 [17] and Seungsin Lee [10] investigated the use of polyurethane nanofibers by exploring the effect of electrospinning duration, i.e. areal density of web in protective textiles. ASTM E96 standard was used to measure the water vapor permeability. It was found that, web density, hydrostatic pressure, and tensile strength all enhance with the increase of electrospinning time. On the other hand, water vapor transmission remains almost unchanged. In extension, the author also pointed out that the weight of the conventional PTFE membrane is much higher than PU nanofiber mats, which could be a powerful advantage in sportswear clothing and application. Kang et al. investigated the contrast between PU resin coated fabrics (RCF) and electrospun PU web/fabric (ESF) in terms of breathability and waterproof ability [7]. The desiccant cup method ASTM E96 was used to measure the water vapour permeability. Test conditions were set as 90±5% RH and temperature 40±2°C. They found that the water vapor permeability value of electrospun PU web/fabric is higher than 250 g/h/m2. This value tells about the high level of water vapor permeability for waterproof fabrics. Polyurethane resin coated fabrics have water vapor permeability 13.45 to 64.40 g/h/m2 in range; this value is seriously lower than the electrospun PU web/fabric. As far as water resistance is disturbed, polyurethane resin coated fabric has a significantly higher water resistance value than PU web/fabric. A value of water resistance 36.5 cm H_2O occurs in polyurethane web/ fabric. However, fiber/pore size and web thickness enhance the water resistance property of electrospun polyurethane web/fabric. In addition, at the same thickness polyurethane resin coated fabric has a higher weight than electrospun PU web/fabric (ESF), because a lot of pores and an open structure present in electrospun PU web/fabric (ESF). In terms of thermal comfort properties, Hae Wook et al. investigated the difference between PTFE-coated clothes and electrospun polyurethane nanofiber laminate. Desiccant cup method with standard ASTM E-96 is used to measure the water vapor transmission rate. Especially notable was that the author examined the effect of relative humidity and temperature on breathability of nanowebs and the author find that the increase in temperature and relative humidity result in rise of water vapor transmission rate of all samples. However, at the higher temperature and humidity the gap of water vapor permeability between polytetra flouro ethylene laminates and polyurethane nanowebs increases seriously. Therefore, Hae wook et al. was concluded that poly tetra fluoro ethylene laminate is more effective at low temperature and low humidity gradient the clothing than nanoweb laminate in terms of water vapor permeability. This may be another advantage of nanofiber. That’s why nanofibre is used as barrier material and filtration compared with the conventional ones.

2.4 Electrospinning technique

Electrospinning is one of the most popular fabrication techniques of producing nanofibres. In recent years, electrospinning has gained tremendous attention of producing nanofibers with diameter nanometer to greater than 5μm, due to its capability of producing polymer fibers. The basic electrospinning set-up is shown in figure 2. This is simple and it consists of a metering pump, syringe, needle, high voltage supply and a collector plate. The polymer solution is pumped through the tip of the needle and an electric field is applied to the tip of the needle and collector plate by applying high voltage supply. When the surface tension in the liquid droplet is overcome by the force of electric field it becomes unstable and the liquid jet is ejected. Then the nanofibers are collected on to the collector surface. A stationary collector results in randomly oriented fiber mats while rapidly rotating collector result in aligned nanofibers.

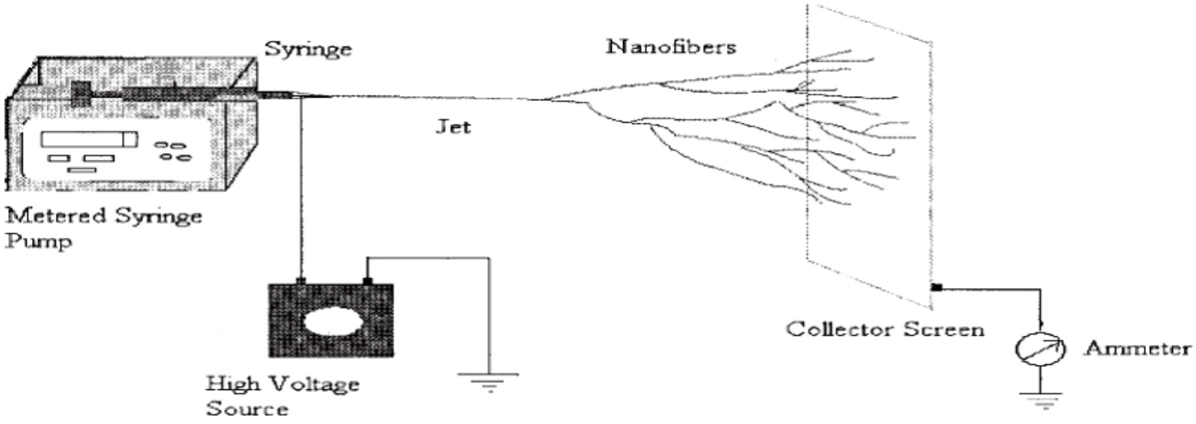


Figure 2 Set-up of electrospinning process (Subbiah et al., 2005)

Electrospinning parameters affect the morphology of nanofibers [68]. The parameters such as viscosity, concentration of solution, voltage, distance, flow rate, temperature and humidity. A problem is remaining with only one needle in regular electrospinning is that the productivity is very low, but nanofibers can be successfully spun. Yang et al. solve this problem and proposed a non needle spinneret & a spinneret with multiple needles to get higher productivity. In multiple needle spinnerets, the needle blocking problem may arise, but in needleless electrospinning no problem is created to increase the productivity [68].

2.5 Three layered structure

V. Parthasarathi & G.Thilagavathi stated that fabric thickness and weight restrict the air and water penetration because more no of fibers are present in the fabric per unit area. More no about fibers generate high entanglement and compact structure of fabric. And because of this compact structure water and air penetration reduces.

2.6 Polyurethane nanofibers for protective textiles

Polyurethane nanofibers with high surface area have many applications. Researchers have developed various methods of producing nanofibers. Polyurethane is a widely used elastomer in coatings, adhesives, binders, air filters, protective textiles, sensors, and in biomedical fields viz. biomedical device, tissue engineering, wound dressing materials, antimicrobial filters, and many more [11-13]. Polyurethane (PU) electrospun mats are very promising in tissue engineering [12,13], protective clothes [7,17], biosensor [18], nanofiltration [18], smart textiles, nanocomposites and may more [10,11,20]. Asghar sadighzadeh et al. [3], showed that on improvement of waterproof breathable properties using varying parameters (concentration of polymer and voltage) and find PU fiber web is best than PAN and PES. Some researchers have focused on production of Polyurethane nanofibres from using different solvents and show the influence of solvents properties on morphology [11] and mechanical properties of Polyurethane electrospun fibre mats. Gorji et al. 2012 [17] showed that PU electrospun mat as good windproof membrane with acceptable water vapor transfer ability and low air permeability. In researches reported by Ahn et al. and Yoon et al. 2011 [6], the electrospun PU nanofibrous membrane showed a better WVP than the PTFE membrane and higher water resistance than nylon and polyester waterproof fabrics. However, it was still of lower air permeability rate, which affects the cloth comfort [1].

2.7 Silica nanoparticles

Silica is the attractive material for fabric coatings because it is characterized by its nontoxicity, biocompatibility, chemical inertness, thermal stability, controllable pores, tunable surface, harmless and inexpensive [25]. Mesoporous silica materials have a high surface area, large pore volume, tunable pore structure and well defined surface quality for modification [36, 38]. The textiles modified by silica nanoparticles coating showed excellent water repellent property and self cleaning behavior [39]. The nano-sized silica acts as reinforcing agent to improve the hardness, strength [41], and thermal stability [42] of the polymers [43]. Mesoporous silica nanoparticles are used in drug delivery [44], biomedical applications and in tissue regeneration [38]. At the present time silica nanoparticles are manufactured as additives for a film forming agent, fecade coating, and biological medicine [49, 51]. Yi Chen et al. reported that the modification of PU leather coatings with Nano- SiO_2, to improve the breathability or wear comfort of PU leather. C.-H. Xue et al. reported the complex coating of amino and epoxy functionalized silica nanoparticles with epoxy-functionalized cotton textiles to generate a dual-size surface roughness and super hydrophobic surfaces have prepared. Qinwen Gao et al. was reported the use of silica sol and hexadecyltrimethoxysilane (HDTMS) to impart extremely high hydrophobicity to both cotton and polyester fabrics [54]. Bae et al. and M. Zhang et al. prepared superhydrophobic cotton fabrics. Surface roughness are created by the combination of the silica nanoparticles and a cost-effective water-repellent agent [55]. Xu et al. manufactured the superhydrophobic surface on cotton fabrics. The surface roughness created by combining the silica nanoparticles, zinc oxide nanorods and low surface energy modified by DTMS [56].

2.8 Cotton fabric for protective textiles

Cotton, cotton-polyester and polyester plain woven or tightly woven fabrics have high protection [2, 4]. Cotton fabric has good absorbency. So it can absorb perspiration easily. Yu et al. 2007 [40] prepared the superhydrophobic surfaces by the sol-gel method. The sol–gel method based on nanosilica and perfluorooctylated quaternary ammonium silane coupling agent, is used for the preparation of superhydrophobic cotton fabric surfaces. This is the combined technique in which these two components help to introduce nanoroughness and surface energy lowering. In another study, Bae et al. 2009 [56] studied that for producing super hydrophobic cotton fabrics. Perfluoroacrylate based water repellent agent is added in a nanocomposite coating of silica nanoparticles. 0·1 wt % amount of noneco-friendly fluoro compound reduces by the nanoroughening and surface tension lowering agent. Silica nanoparticles cannot wind to cotton surface. They are not durable with the fabric. To adhere to cotton surface, nanosilica can be used as a component for nanocomposite coating. An excellent superhydrophobicity (>170◦), is created by applying Amino functionalized silica nanoparticles on epoxy functionalized cotton fabric. Xue et al. 2009 [53] produced nanoroughness on fabric surface. This roughness is very durable and robust because the strong bond is created between the particles and fiber during the fictionalization of silica and cotton surface.

2.9 Polyester for protective textiles

Borom Yoon and seungsen Lee, 2011 [6] use hundred percent polyester fabrics as substrate fabric. Tightly woven microfilament fabrics are durable and lightweight due to their compact structure and small pores. They have high waterproofness and drapeability but lower breathability. For increasing durability and strength of synthetic fibre, microfibers are used to make a fibre [Hatice et al.]. Nylon and polyester fibres are made of microfibers [Smith et al, 2007]. Polyester fabric has good drapeability, windproofness and strength than nylon because polyester is found in more fine filaments than nylon. [Hatice et al]. Production of microfibers possible in three types such as melt, dry and wet spinning methods and ultrafine fibers produce by direct and conjugate spinning methods [Purane and Panigrahi, 2007].

CHAPTER 3: EXPERIMENTAL

3.1 Materials

Polyurethane is selected for electrospinning, was purchased from local market of Delhi. Dimethylformamide (MW 73.09) obtained from High Purity Laboratory Chemicals Pvt. Ltd., was used as solvent for Polyurethane. Silica nanoparticles (SiO_2 MW 60.08) in powder form, obtained from Sisco Research Laboratories Pvt. Ltd. (Maharashtra, India). Cotton and polyester 2/2 plain weave fabrics are used for 03 layered structure, obtained from local market of Delhi. The weight of cotton fabric is 111g/m^2 and polyester is 92 g/m^2.

3.2 Methods

3.2.1 Spinning solution preparation

Silica nanoparticles in powder form are used for hydrophobicity. Silica nanoparticle dispersion was prepared by sonicating SiO_2 nanopowder in DMF, for 20 minutes using a low power bath sonicator. 0.5% and 1% silica nanoparticles are used for solution preparation.

3.2.2 Particle size analysis

Particle size analyzer (microtrac S 3500) was used for particle size analysis. 500 ml aqueous solution of silica nanoparticles was added to the quartz cell of the particle size analyzer. Measurements were taken in triplicates at 90° to the incident light source.

3.2.3 Solution properties

The viscosity of a solution is measured by Brookfield (DV-II + Pro) Viscometer. Viscosity measurement with respect to the time S62 spindle is usable at 10 RPM and the temperature is maintained at 32.7°C. And viscosity measurement with respect to temperature spindle is used at 10 RPM at varying temperature 35°C-100°C. And Viscosity-average molecular weight of polymer was identified by viscometric measurements using an Ubbelohde Capillary Viscometer. This value was calculated from $[\eta] = KM\alpha$ equation, where $K= 3.64x10^{-4}$ (dm^3/g) and $a = 0.71$ determined in DMF and polyurethane solution at 25°C. [58]

3.2.4 Electrospinning condition

The nanofibrous mats were prepared using electrospinning machine Royal Electro Spinner, India equipped with collecting drum. The collector was covered with aluminum foil to collect Polyurethane nanofibrous mat, for preparing uniform fibers without beads, the varying parameters such as acceleration voltages 13 KV, 14 KV and 15 KV, spinning distance 8 cm, 15 cm and 22 cm, concentration of solution 11%, 12% and 13% and flow rate 0.6 ml/hour was studied.

3.2.5 Preparation of Polyurethane or polyurethane nanosilica based nanofibrous web

The optimal electrospinning condition was examined for concentration of solution, applied voltage, tip of the needle to collector drum, flow rate of automatic syringe pump etc. The electrospun web was collected onto the aluminum foil and after optimization of parameters; this layer is directly electrospun on to the fabric substrate.

3.2.6 Fiber Analysis

Morphology of polyurethane and polyurethane nanosilica based nanofibrous mats was examined by Scanning Electron Microscope (SEM, Hitachi S-3700N SEM, Germany) a voltage of 15KV. All samples were sputter coated with gold prior to SEM analysis. Fiber diameter was measured by image software called Image J (NIH, http://rsbweb.nih.gov/ij/), based on images obtain from SEM analysis. As many as 30 fibers were selected for each sample on different positions. Nanofiber diameter of each sample was estimated from statistics from those fibers.

3.2.7 Preparation of two layer fabric structure

In two layer fabric structure cotton fabric is used as substrate fabric. Polyurethane or polyurethane/ nanosilica based nanofibers are directly electrospun on to the fabric substrate.

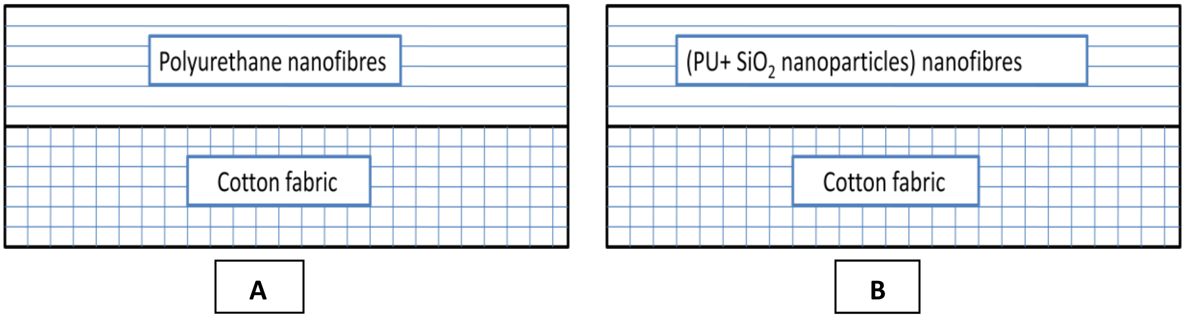


Figure 3: A, B-Two layered fabrics

3.2.8 Preparation of three layer fabric structure

In three layer fabric structure (C), cotton fabric is used as substrate fabric. Polyurethane/ nanosilica based nanofibers are directly electrospun on to the fabric substrate. The third layer is of polyester fabric, which is stitched on to the two layer of fabric (B).

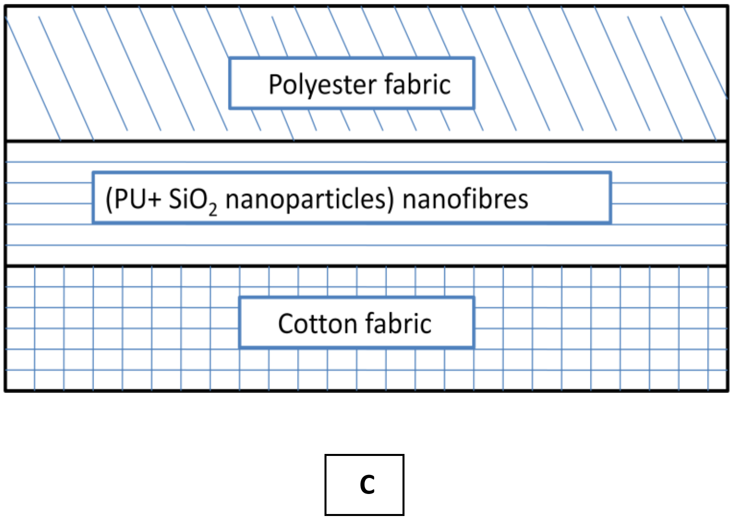


Figure 4: C-Three layered fabric

3.2.9 Contact angle

Contact angles were measured through DSA 100 Goniometer from Kruss Inc., Germany. The measurements were made at 25°C and 65% relative humidity with distillate water as test liquid with drop volume of 6 microliter. Three independent measurements were made for each sample. The mean values and standard deviations were then calculated.

3.2.10 Water vapor transmission rate (WVTR)

The upright cup method was used for measuring the WVP. [59] Four tests of each sample were carried out. And the mean value was recorded. Finally, WVP was determined using the following equation: WVP = M /A. t

Where WVP is water vapor permeability (g_day−1_m2), M is weight reduction in one day. A is area of the sample that is in contact with air (m2), and t is the duration of testing in hours.

3.2.11 Air permeability test

WIRA air permeability tester with test method IS: 11056-84 (RA 2006) was used to measure the air permeability. Sample size is 0.25m x full width. Ten tests are carried out for each sample.

3.2.12 Water wicking test

In this test we take 100 ml of beaker and 50 ml of distilled water in it. 3x3 cm of samples is cut to the measurement. Samples are retained on the water surface carefully. Time of wicking was recorded by stop watch. Five tests of each sample are carried out and the mean value is calculated.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Solution properties

For suitable polymer concentration, we investigate the effect of time and temperature on a polymer solution by using a Brookfield Viscometer. Viscosity of solution increases with the increase in time and decreases with increase in temperature. The viscosity average molecular weight of polyurethane is also determined. Actually viscosity, concentration of the solution and polymer molecular weight is related to each other. And they have an important effect on morphology [60-66]. The viscosities of solution are measured at four different concentrations 0.01%, 0.05%, 0.1%, and 0.5%. Viscosity of polyurethane solution is increasing with the increase in concentration linearly and the molecular weight is found in the range of fiber forming polymer.

4.1.1 Effect of time and temperature on viscosity of Polyurethane solution

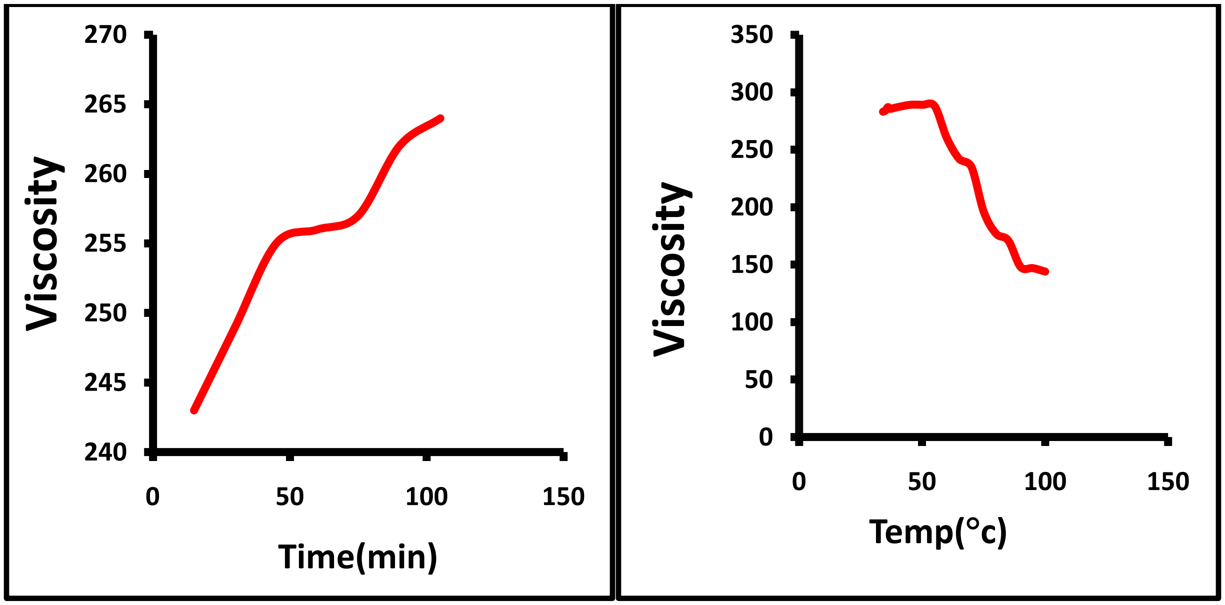


Figure 5: Effect of time and temperature on viscosity of Polyurethane solution

4.1.2 Viscosity average molecular weight determination of Polyurethane

Time (t) **to = 1.1**	**Relative viscosity ($\eta_r = t/t_o$)**	**ln η_r**	**Conc.**	**Specific viscosity $\eta_{sp} = \eta_r - 1$**	**Reduced viscosity (η_{sp}/c)**	**intrinsic viscosity (ln η_r/c)**
1.32	1.2	0.1823	0.01	0.2	20	18.23
1.34	1.218	0.1972	0.05	0.218	4.36	3.944
1.35	1.227	0.2046	0.1	0.227	2.27	2.046
1.47	1.336	0.2896	0.5	0.336	0.672	0.5792

Table 1: Viscosity average molecular weight determination of Polyurethane

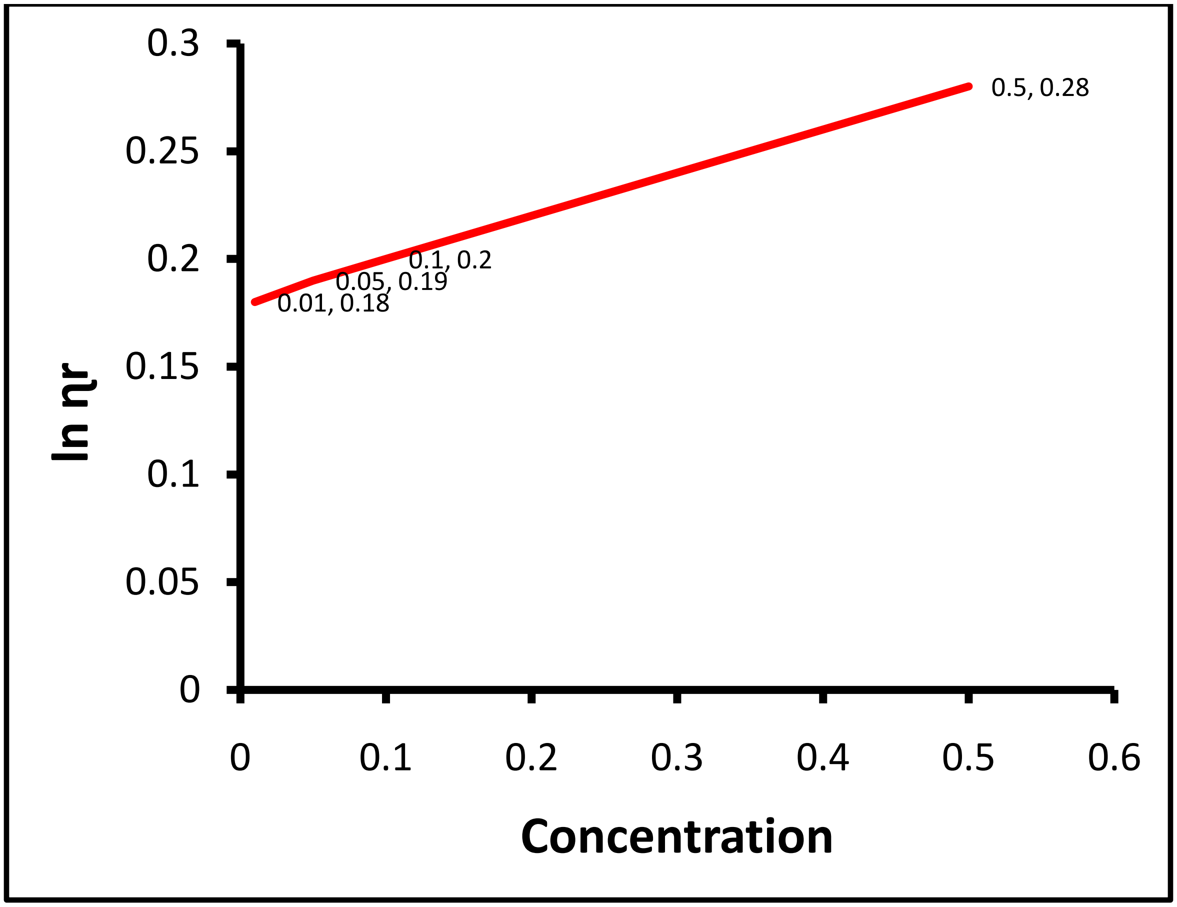


Figure 6: Relation between concentration and ln ɳr

Calculation

- $[\eta] = KM^{\alpha}$
- $[\eta] = 3.64 \times 10^{-4} M^{0.71}$.
- $0.18 = 3.64 \times 10^{-4} M^{0.71}$.
- $[M] = [0.18/3.64 \times 10^{4}]^{1/0.71}$.

$[M] = 6{,}231$

4.2 Preparation of Polyurethane nanofibrous mats

In order to prepare Polyurethane electrospun nanofibers in optimum conditions, the effect of variable parameters including concentration of solution, voltage and collector plate distance was varied and the results are discussed as follows.

4.2.1 Effect of nozzle and collector plate distance

To study the effect of nozzle and collector plate distance, the polyurethane solution was electrospun at a different collection distance, such as 8cm, 22cm and 15cm, under constant voltage 15KV, concentration 13% and flow rate 0.6 ml/h. The fiber morphology and diameter obtained at a different collection distance are shown in Figure A, B, and C. Diameter of nanofibre decreases with distance, because the flight time of nanofibre to the collection plate will reduce. [67] At collector plate distance of 8 cm highest fiber diameter and lower contact angle are obtained. At 22 cm distance, difference in diameter of nanofibres is larger, microfibers are also obtained here. And because of the surface irregularity, contact angle increases. At 15 cm distance fiber diameter is less than more adhesion bonding. And these bonding pin the motion of water and observed contact angle increases.

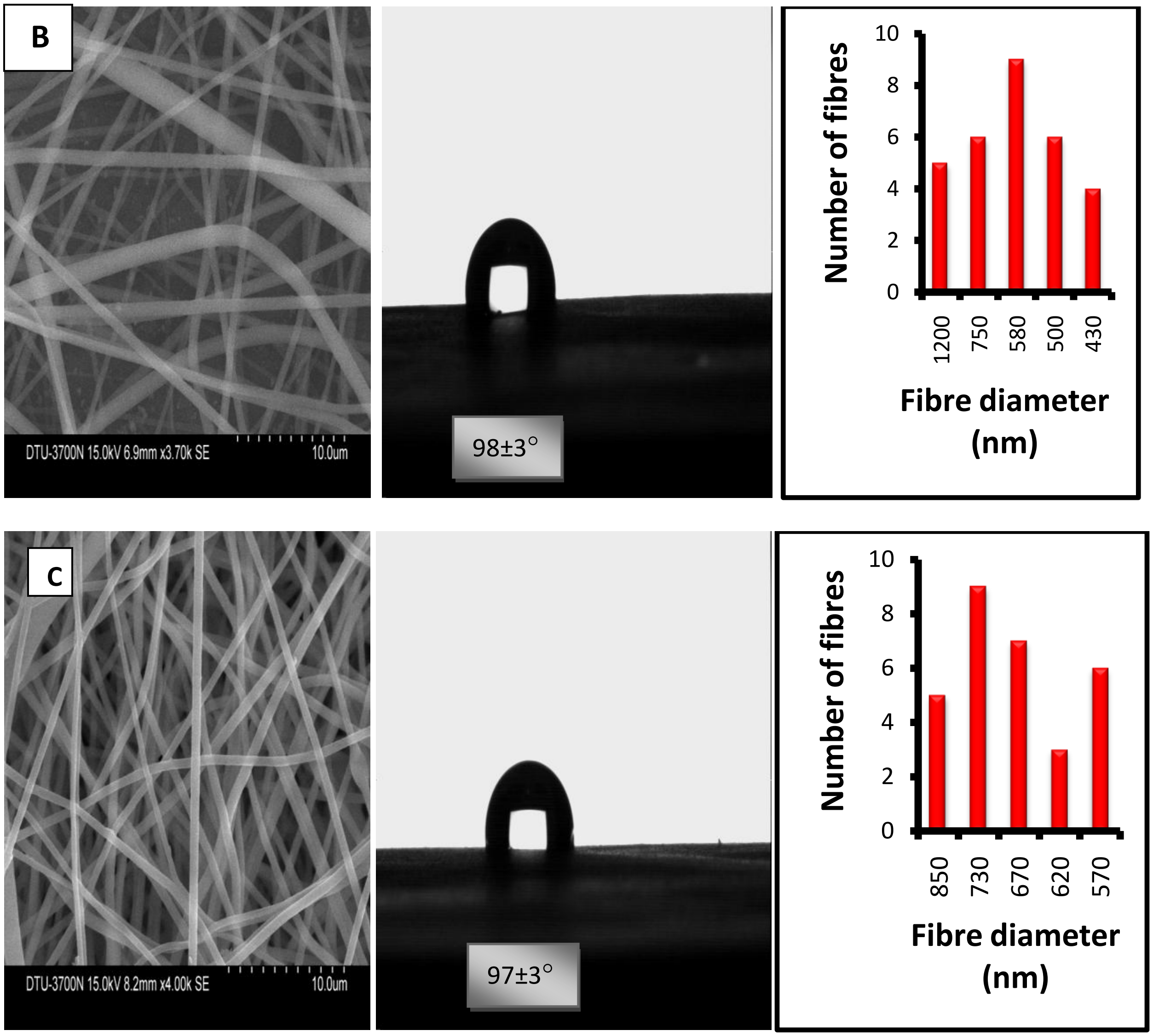
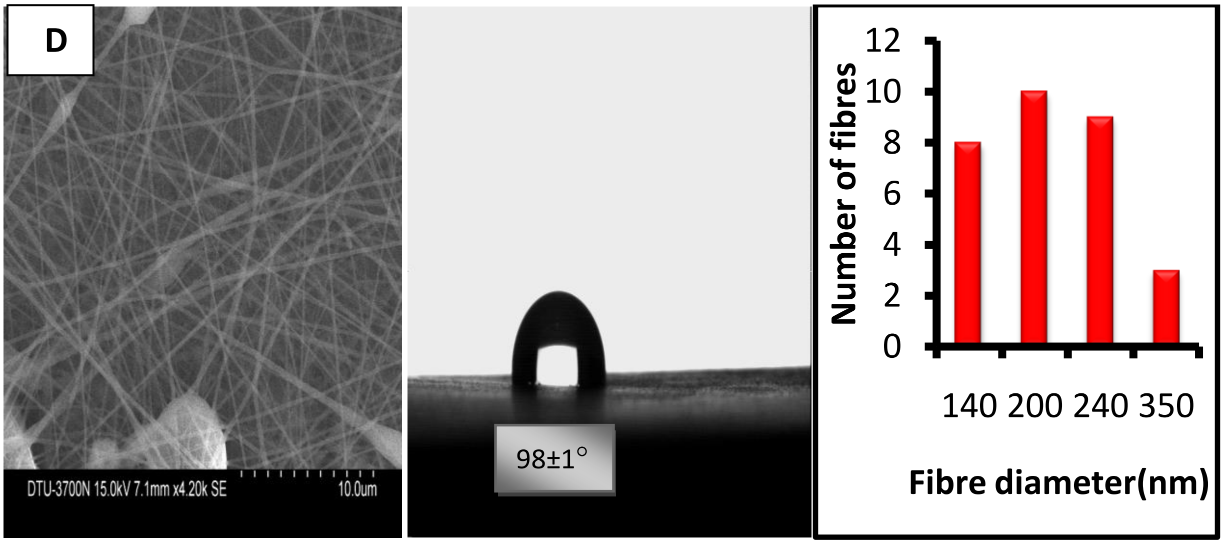


Figure 7: Scanning electron microscope, contact angle and nanofibre diameter of, Sample A- Distance 8cm, conc13wt/v%, voltage-15 kv, Flow rate-0.6ml/h, Sample B- Distance 22cm, conc13wt/v%, voltage-15 kv, Flow rate-0.6ml/h and Sample C- Distance 15cm, conc13wt/v%, voltage-15 kv, Flow rate-0.6ml/h.

4.2.2 Effect of concentration of solution

The effect of concentration of polymer solution on the morphology, the Polyurethane solution was electro spun at three different concentrations (13%, 11% and 12%). The SEM images of Polyurethane at constant voltage 15 KV, nozzle and collector distance 15 cm and flow rate of 0.6 ml/hour are shown in figure C, D and E. It was observed that the diameter of nanofiber at concentration 11% is finer than 12% but the bead formation is higher. The nanofibers formed at concentration 12% and 13% had a negligible bead formation compared to 11%. Because of suitable concentration, smooth nanofibres are obtained at 12% and13%. Fiber diameter is increasing with the increase in concentration because of the high concentration, polymer content in the solution increases, so the thicker fiber is formed. [67]



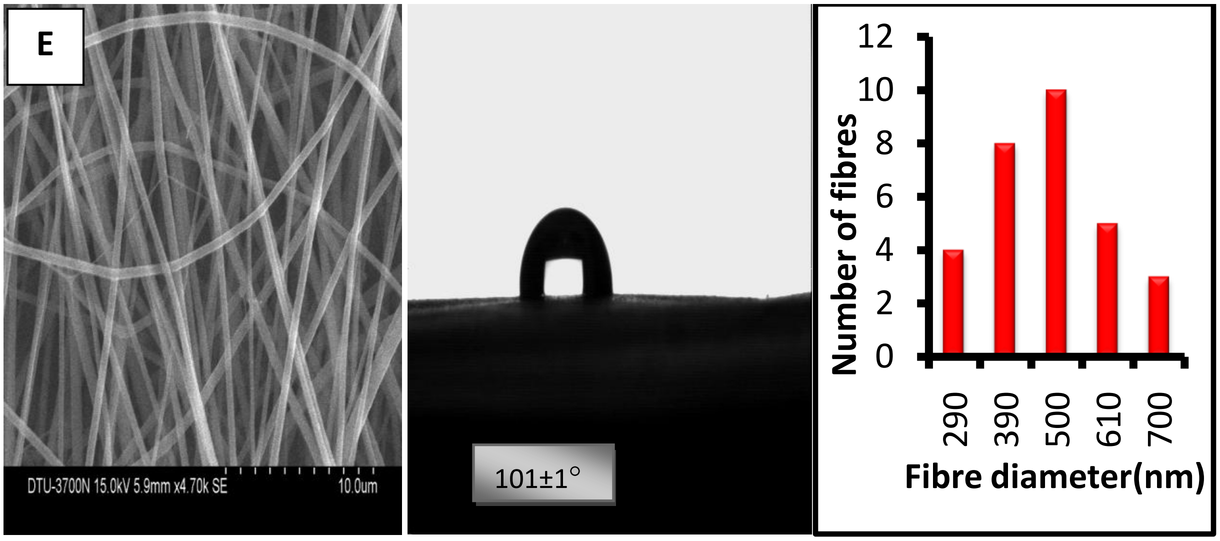


Figure 8: Scanning electron microscope, contact angle and nanofibre diameter of, Sample D-conc11wt/v, distance-15cm, voltage-15 kv, flow rate-0.6ml/h and Sample E-voltage15 kv cons. 12wt/v%, distance 15cm, flow rate 0.6ml/h

4.2.3 Effect of acceleration voltage

The SEM images of polyurethane nanofibres prepared at 15 cm, 0.6 ml/HR, 12% and varying voltages including 15 KV, 14 KV and 13 KV are shown in Figure E, F and G. The average diameter and the contact angle are also shown in Figure. The corresponding average diameter of nanofiber decreases with decrease in voltages. Because the flight time of electrospinning jet may influence the diameter of electrospinning jet. A shorter flight time will allow less time for the fibers to stretch and elongates before it is deposited on the collection plate. Thus at higher voltage, raised acceleration of the jet and the strong electric field may decrease the flight time of the electrospinning jet which may favor the formation of thicker fibers. The contact angle decrease with increase in fiber diameter while increase with increase in surface roughness created by the morphology of nanofibres.

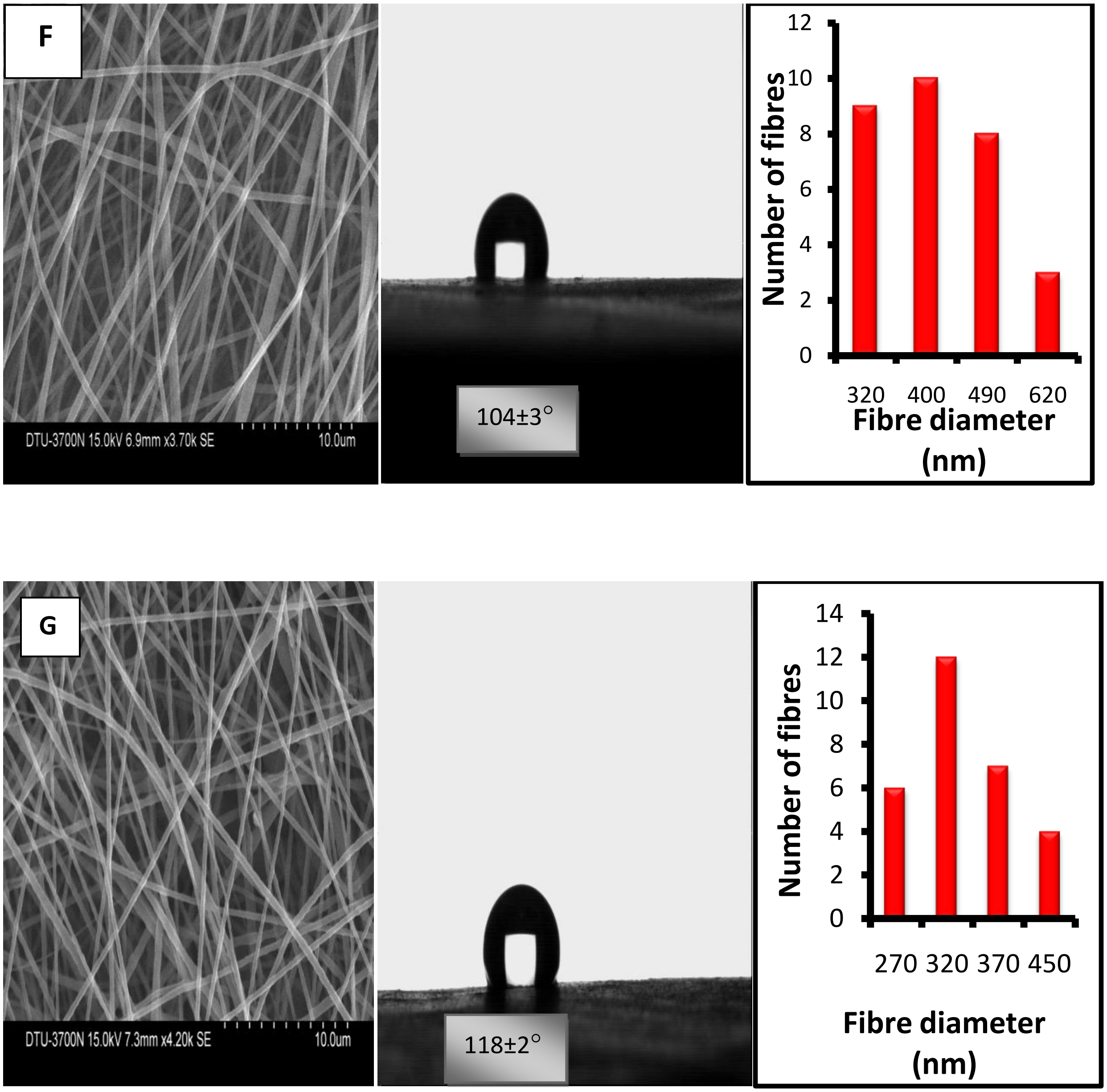


Figure 9: Scanning electron microscope, contact angle and nanofibre diameter of, Sample F-voltage14kv, conc12wt/v%, distance15cm, flow rate0.6ml/h and Sample G-voltage13kv, conc12wt/v%, distance15cm, flow rate0.6ml/h.

4.3 Particle size analysis

According to the analysis, the average size of nanoparticles is 0.313 micrometers. These nanoparticles can easily disperse in PU solution and can create desired nanoroughness on the fabric surface.

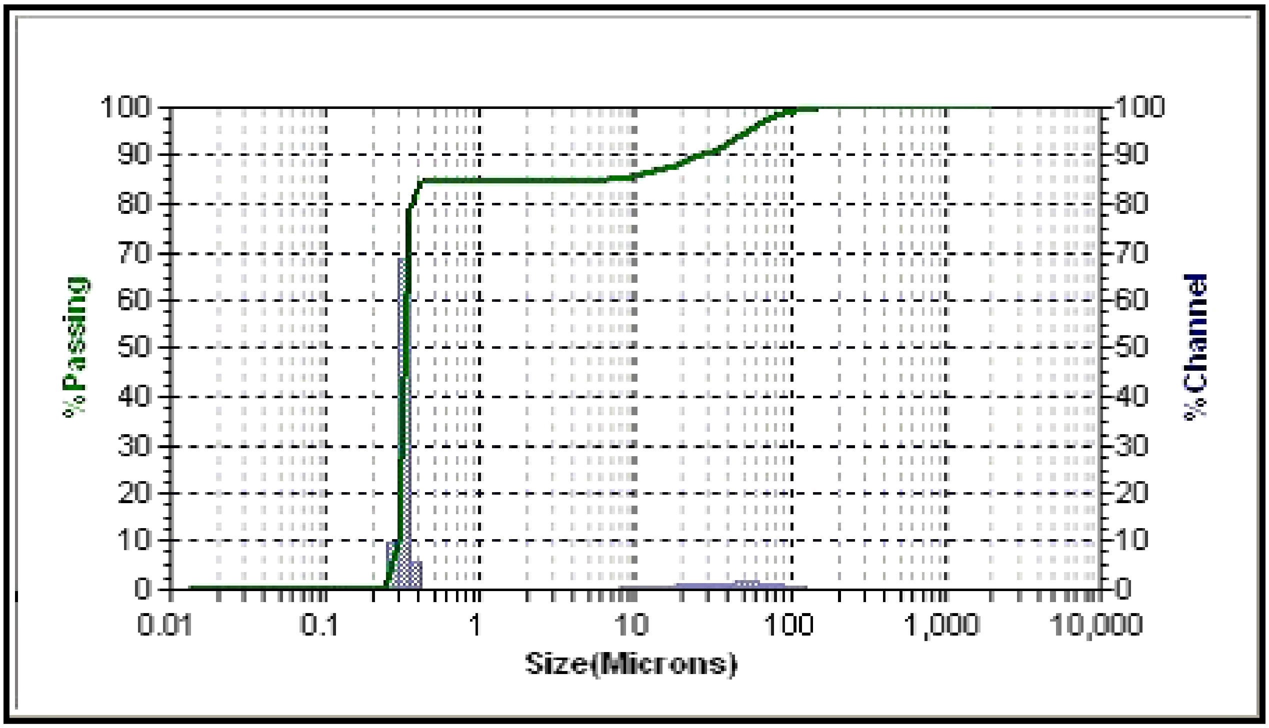


Figure 10: Particle size analysis

4.4 Effects of nanosilica on surface roughness

Fig H and I show the effect of SiO_2 nanoparticles on the polyurethane nanofibrous mat. Silica nanopaticles creates nanoroughness in non-woven structure, hence observed contact angle increases.

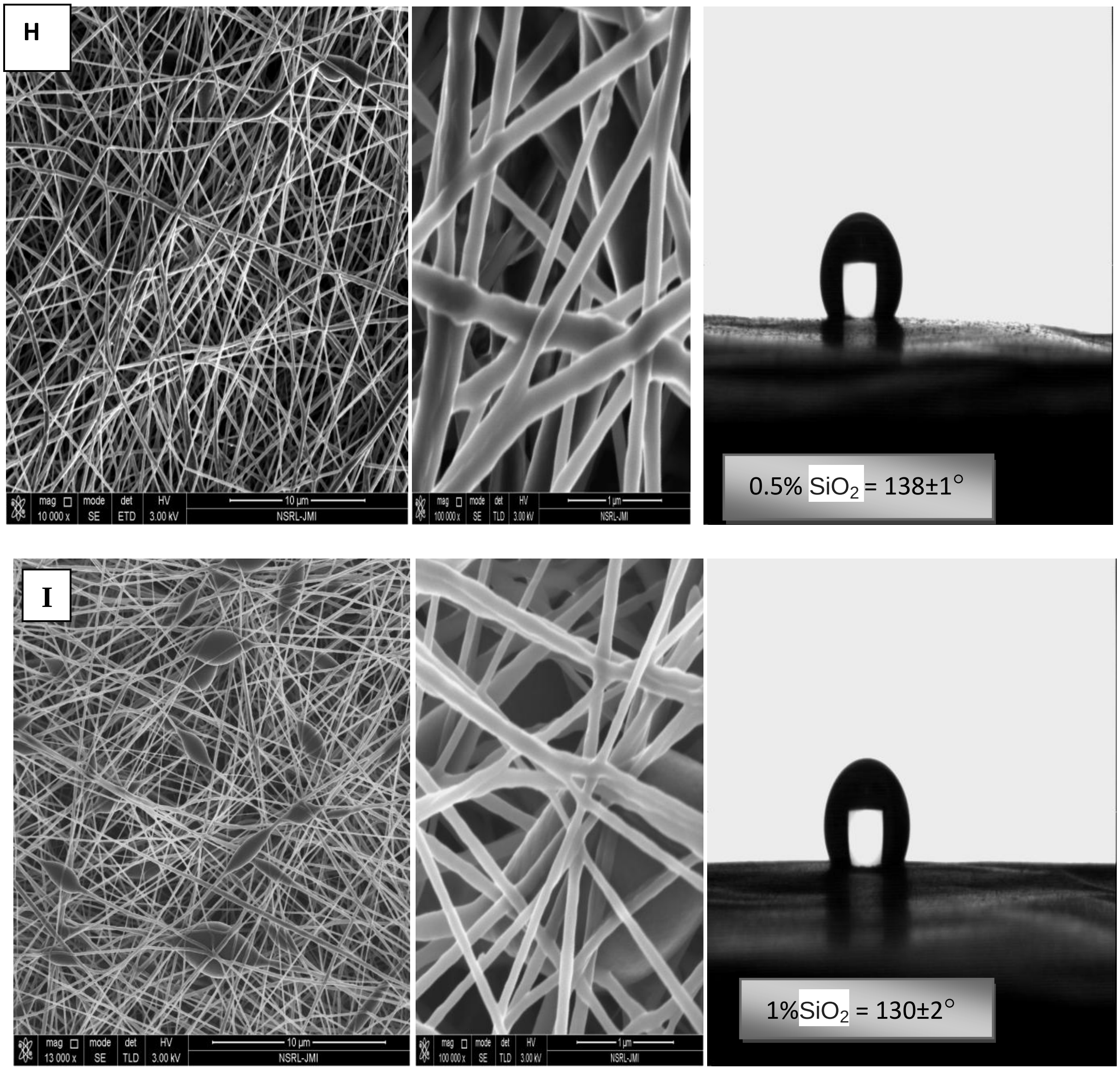


Figure 11: SEM images at different scale 10 µm & 1µm and Contact angle of sample H and I.

4.5 Three layer fabric construction

Number of layers	**Material**	**Thikness (mm)**	**Contact angle**	**WVTR (gm/m²/day)**	**Air permeability (cc/sec/cm²)**	**Water wicking**

First layer (C)	Cotton	0.21	80±1°	115	41.26	No time
Third layer (P)	Polyester	0.15	104±2°	118	99.27	Some time 10-16 sec
02 layered structure						
(CU)	Cotton + PU	0.22	134±3°	114	6.12	No wicking till 24 hours
(CS)	Cotton + (PU + 0.5% SiO_2)	0.23	148±2°	115	8.63	No wicking till 24 hours
03 layered structure (CPS)	Polyester + (PU+0. 5% SiO_2) +cotton	0.36	145±1°	109	8.56	No wicking till 24 hours

Table 2: Performance of prepared waterproof Breathable fabric structures

4.5.1 Contact angle test

Contact angle depends on the nanoroughness of the fabric. Nanoroughness pin the motion of water and observed contact angle increases.

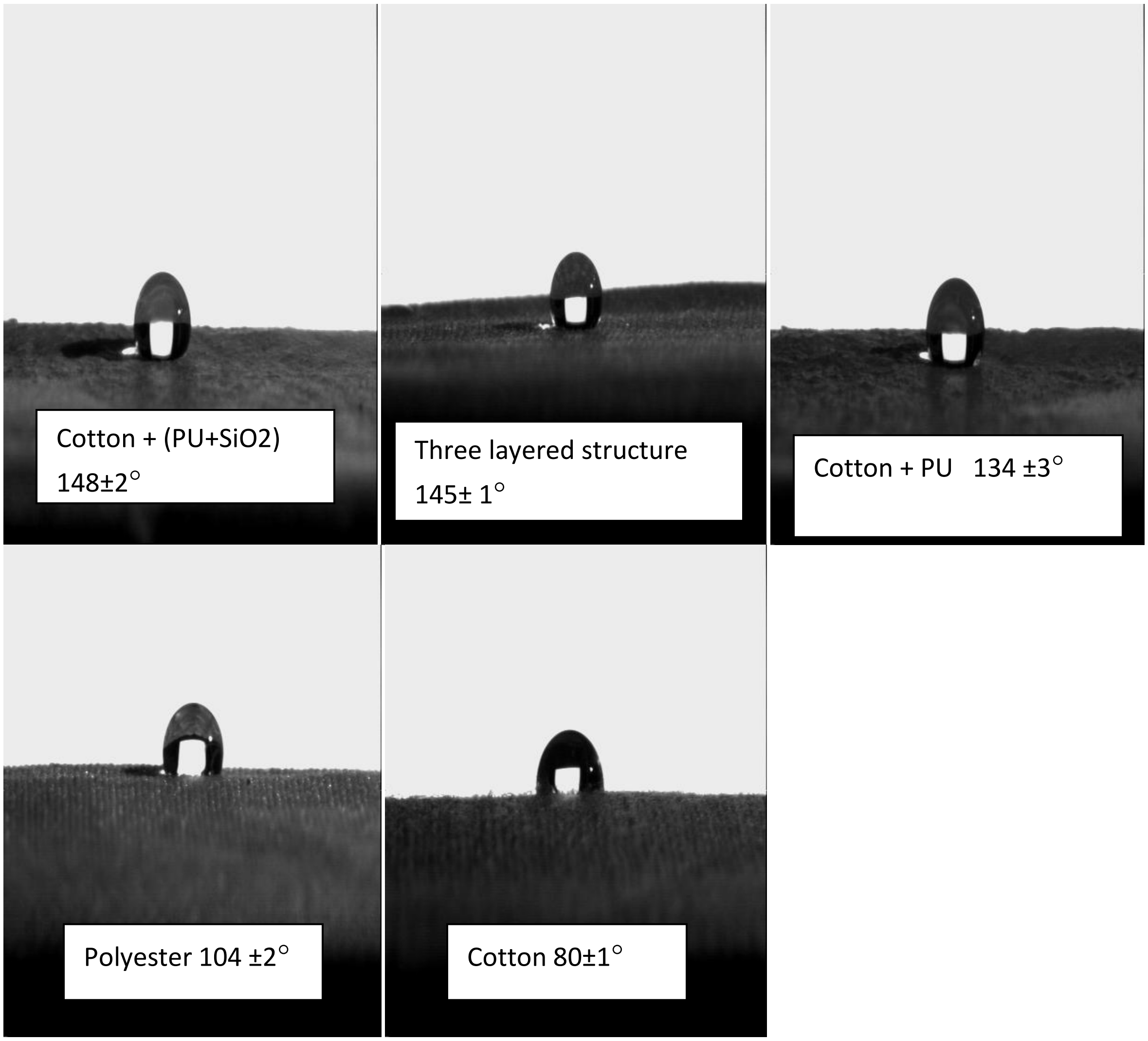


Figure 12: Contact angle of fabric samples

4.5.2 Water vapor permeability test

Water vapor transmission rate is the most desirable feature in waterproof breathable fabrics that allow the transfer of perspiration vapor and heat from the body to the environment and keep the body cool and dry.

Long staple, plied and combed cotton yarns and synthetic microfilaments are used to woven the fabric (Lomax, 1985). Such yarns have high density and the fabric have minimum pores. Very high pressure of air and water is required to penetrate such kind of fabric. Cotton fibres swell when the fabric is dipped into water and the pore size reduces further after wetting. But synthetic filaments do not swell after wetting so further coatings are required in synthetic fabrics to obtain desired results [2].

Cotton fabric has lower water vapor permeability than polyester because there are minimum pores in the cotton fabric. Cotton fabrics absorb moisture and swell while polyester fabrics take negligible moisture and do not swell. So the pores became reduces in cotton fabric and it has lower water vapor permeability. Polyester fabric has inherent water repellent properties but high water vapor permeability.

CU has lower water vapor permeability than CS because silica nanoparticles can not completely wind with cotton surface.

V. Parthasarathi & G.Thilagavathi stated that fabric thikness and weight restrict the air and water penetration because more no of fibres are present in the fabric per unit area. More no of fibres generate high entanglement and compact structure of fabric. And because of this compact structure water and air penetration reduces.

In three layered fabric structure, fabric thikness and weight restrict the water penetration because more no of fibres are present in the fabric per unit area. More no of fibres generate high entanglement and compact structure of fabric. And because of this compact structure water penetration reduces.

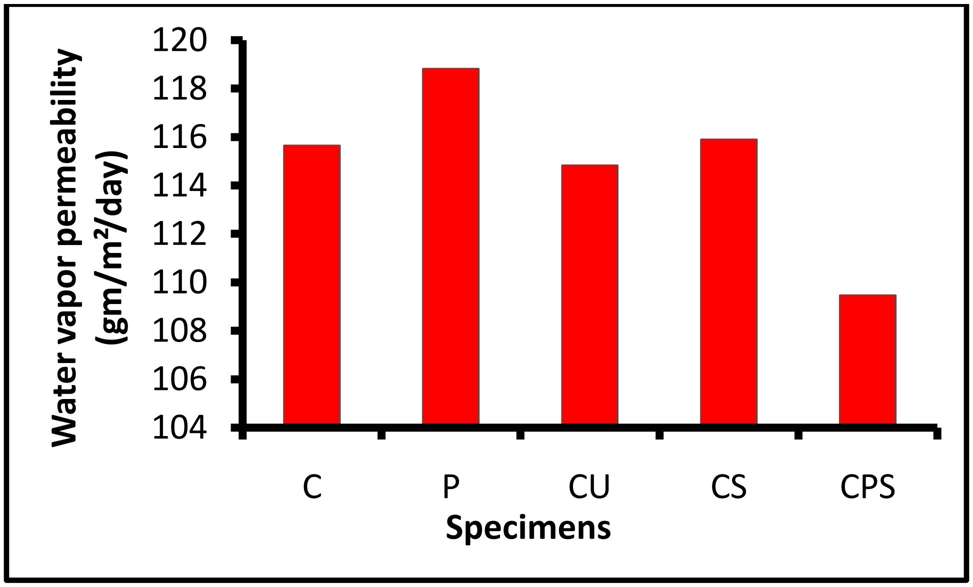


Figure 13: WVTR of fabric samples

4.5.3 Air permeability test

Air permeability is an important factor of thermal comfort that promote the breathing and ventilation functions in apparel.

Cotton fabric has lower air permeability than polyester because there are minimum pores in the cotton fabric. Polyester fabric has inherent water repellent properties, but high air permeability.

Bae et al (2009) studied that for producing super hydrophobic cotton fabrics. Perfluoroacrylate based water repellent agent is added in nanocomposite coating of silica nanoparticles. 0·1 wt % amount of noneco-friendly fluoro compound reduces by the nanoroughening and surface tension lowering agent. Silica nanoparticles cannot wind to cotton surface. They are not durable with the fabric. To adhere with cotton surface, nanosilica can be used as component of nanocomposite coating.

CU has lower air permeability than CS because silica nanoparticles can not completely wind with cotton surface. Silica nanoparticles are not durable when applied high pressure of air to the fabric.

Boron Yoon and Seungsin Lee, 2011 [6] stated that fabric weight, thickness, pore size and amount of voids present in the material affects the water and air penetration of the fabric.

In three layered fabric, the fabric thikness and weight restrict the air penetration because more no of fibres are present in the fabric per unit area. More no of fibres generate high entanglement and compact structure of fabric. And because of this compact structure air penetration reduces.

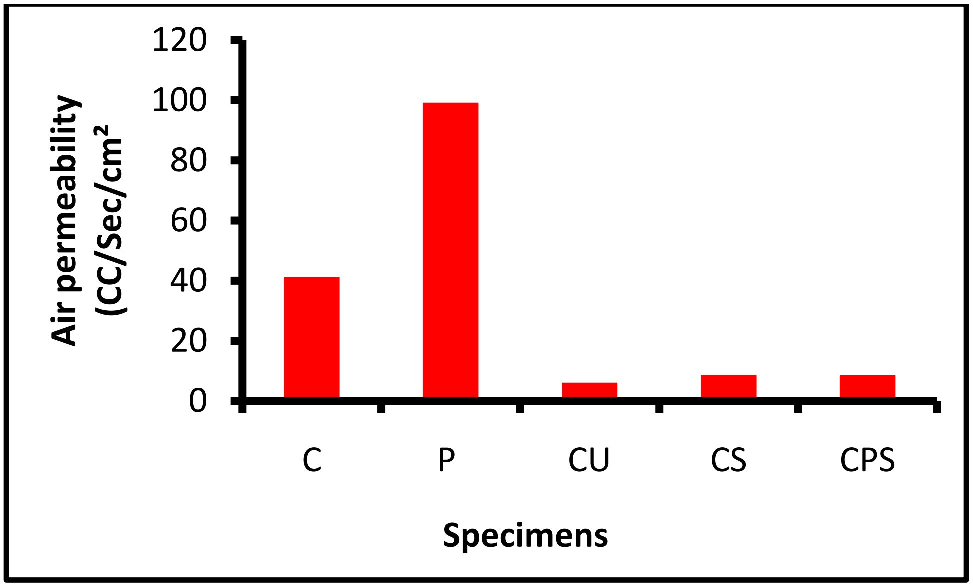


Figure 14: Air permeability test of fabric samples

4.5.4 Water wicking test

Water wicking plays a very important role in determining comfort, dyeability, liquid filteration and moisture transportation behavior of fabric through the phenomenon of capillary.

In this test cotton fabric sample takes no time of wicking. It absorb the water instantly and sink, while polyester fabric takes some time of wicking then it is also sink. Other remaining fabrics have no wicking and float on the surface. This measurement is recorded till 24 hours. This is because these fabrics have tiny pores, but fiber randomness in their structure locks the water penetration. While the substrate fabric (cotton fabric) present in these fabrics absorbs the water easily. Hence, these fabrics have comfort and moisture transfer behavior with hydrophobic surfaces.

CONCLUSION

This experiment was carried out with the aim of developing desired waterproofness and breathability of the fabric. The results show that the viscosity of polymer is increasing in concentration of solution linearly. Solution viscosity increases with respect to time and decreases with respect to temperature. Molecular weight of polymer is [M] = 6,231. This is in the range of fiber forming polymer. The nanofibre diameter was found nanometer to micron range. The nanofibre diameter increase with increase in concentration and voltage and decrease with an increase in distance and the contact angle of nanofibrous webs increase with decrease in diameter. Optimized electrospun nanofibers were developed to achieve the desired results. In PU optimization contact angle varies from 79±3° to 118±2°. And PU nanosilica based nanofibers were successfully obtained with maximum contact angle 138±1°. In waterproof breathable fabrics, polyester fabric has high waterproofness and breathability than cotton. Silica nanoparticles improve the waterproofness and breathability both in CS fabric and CPS fabric. CU fabric has lower waterproofness and breathability.

The results of this investigation indicate that the new generation of nanofibrous materials has a good potential for application in waterproof breathable fabrics.

REFERENCES

1. Golchehr Amini, Samira Samiee, Ali Akbar Gharehaghaji, Farideh Hajiani, Advances in Polymer Technology, 21568, 1-9, (2015).

2. Bakshi, Aditi S., "Development and Study of Waterproof Breathable Fabric Using Silicone Oil and Polyurethane Binder" (2015).

3. Asghar sadighzadeh, mahdi valinejad, akber gazmeh, behzad rezaiefard, Polym. Sci, 1, 143, (2016).

4. A. Richard Horrocks, Subhash C. Anand, “Handbook of technical textiles”, 2, 27-52, (2016).

5. S.K. Chinta and Darbastwar Satish, International Journal of Recent development in engineering and technology, 3, 16-20, (2014).

6. B.Yoon and s.Lee,fibres polym. 12, 57 (2011).

7. Y. K. Kang, C. H. Park, J. Kim, and T. J. Kang, fibres polym.8, 564 (2007).

8. Mondal, S.; Hu, J. L. J Membr Sci, 274, 219 (2006).

9. Fan, J.; Hunter, L. Engineering Apparel Fabrics and Garments; Woodhead: Cambridge, UK, (2009).

10. Seungsin Lee, Inc. J Appl polym sci, 114; 3652-3658 (2009).

11. S. Mondal, Polym. Adv. Technol,25 179–183 (2014).

12 J. H. Yang, N. S. Yoon, J. H. Park, I. K. Kim, I. W. Cheong, Y. L. Deng, W. Oh, J. H. Yeum, J. Appl. Polym, Sci. 120, 2337–2345 (2011).

13. J. P. Theron, J. H. Knoetze, R. D. Sanderson, R. Hunter, K. Mequanint, T. Franz, P. Zilla, D. Bezuidenhout, Acta Biomater. 6 (7), 2434–2447(2010).

14. Bergmeister, H.; Schreiber, C.; Grasl, C.; Walter, I.; Plasenzotti, R.; Stoiber, M.; Bernhard, D.; Schima, H. Acta Biomater., 9, 6032 (2013).

15. Amna, T.; Hassan, M. S.; Sheikh, F. A.; Lee, H. K.; Seo, K. S.; Yoon, D.; Hwang, I. H. Appl. Microbiol. Biotechnol. 97, 1725,(2013).

16. Jia, L.; Prabhakaran, M. P.; Qin, X. H.; Kai, D.; Ramakrishna, S. J. Mater. Sci., 48, 5113 (2013)

17. Gorji, M.; Jeddi, A. A. A.; Gharehaghaji, A. A. J. Appl. Polym. Sci. 125, 4135 (2012).

18. Wang, N.; Burugapalli, K.; Song, W. H.; Halls, J.; Moussy, F.; Ray, A.; Zheng, Y. D. Biomaterials, 34, 888 (2013).

19. Wang, N.; Raza, A.; Si, Y.; Yu, J. Y.; Sun, G.; Ding, B. J. Colloid Interf. Sci, 398, 240 (2013).

20. Wentao Hao, Caiping Fang, Jixian Yu, Liang Zhang, Teng Xue, Wen Yang, J. Appl. Polym. Sci., 131, 40902 (2014).

21. Satoru Kidoaki, Il Keun Kwon, Takehisa Mats, J Biomed Mater Res Part B: Appl Biomater, 76B: 219–229 (2006).

22. Z.-G. Shi et al. / Materials Chemistry and Physics 126, 826–831 (2011).

23. A.B.D. Nandiyanto et al. / Microporous and Mesoporous Materials 120, 447–453 (2009).

24. F. Iskandar, I.W. Lenggoro, T.O. Kim, N. Nakao, M. Shimada, K. Okuyama, J. Chem. Eng. Jpn. 34, 1285 (2001).

25. G. Cavallaro, P. Pierro, F.S. Palumbo, F. Testa, L. Pasqua, R. Aiello, Drug Deliv. 11,41 (2004).

26. C. Charnay, S. Bégu, C. Tourné-Péteilh, L. Nicole, D.A. Lerner, J.M. Devoisselle, Eur. J. Pharm. Biopharm.57, 533, (2004).

27. F. Balas, M. Manzano, P. Horcajada, M. Vallet-Regí, J. Am. Chem. Soc. 128, 8116 (2006).

28. K. Cheng, C.C. Landry, J. Am. Chem. Soc. 129, 9674 (2007).

29. J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, K. An, Y. Hwang, C.H. Shin, J.G. Park, J.Kim, T. Hyeon, J. Am. Chem. Soc. 128, 688 (2006).

30. J. Yang, J. Lee, J. Kang, K. Lee, J.S. Suh, H.G. Yoon, Y.M. Huh, S. Haam, Langmuir 24 3417, (2008).

31. R. Mellaerts, J.A.G. Jammaer, M. Van Speybroeck, H. Chen, J. Van Humbeeck, P. Augustijns, G. Van den Mooter, J.A. Martens, Langmuir 24, 8651 (2008).

32. J.M. Xue, M. Shi, J. Control. Release 98, 209 (2004).

33. N.W. Clifford, K.S. Iyer, C.L. Raston, J. Mater. Chem. 18, 162, (2008).

34. M. Bikram, A.M. Gobin, R.E. Whitmire, J.L. West, J. Control. Release 123, 219 (2007).

35. S.W. Song, K. Hidajat, S. Kawi, Chem. Commun. 42, 4396 (2007).

36. Y. Zhu et al. / Microporous and Mesoporous Materials 141,199–206 (2011).

37. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359, 710–712 (1992).

38. Y. Wang et al / Nanomedicine: Nanotechnology, Biology, and Medicine 11, 313–327 321 (2015).

39. M. Rana et al. / Composites Science and Technology 122, 104e112 (2016).

40. M. Yu, G. Gu, W.D. Meng, F.L. Qing, Appl. Surf. Sci. 253, 3669e3673(2007).

41. D.F. Schmidt, E.P. Giannelis, Chem. Mater. 22, 167–174 (2010).

42. S.H. Lee, J. Eur. Ceram. Soc. 29, 3387–3393 (2009).

43. Y. Bao et al. / Journal of Colloid and Interface Science 407,155–163 (2013).

44. Q. He et al. / Biomaterials 32, 7711e7720 (2011).

45. Q. He et al. / Biomaterials 31, 3335–3346 (2010).

46. Z.-G. Shi et al. / Materials Chemistry and Physics 126, 826–8319 (2011).

47. J. Lu et al / Nanomedicine: Nanotechnology, Biology, and Medicine 8, 212–220, (2012).

48. Y. Wang et al / Nanomedicine: Nanotechnology, Biology, and Medicine 11, 313–327 321 (2015).

49. Y. Bao et al. / Journal of Colloid and Interface Science 407, 155–163 (2013).

50. F.C. Zhao, X.R. Zeng, H.Q. Li, J. Zhang, Colloids Surf., A 396, 328–335 (2012).

51. A. Kolodkin et al/ Eur. J. Pharm. Sci. 46, 190–197 (2012).

52. Yi Chen et al/ Fibres and Polymers 11, 1-8, (2010).

53. C.-H. Xue et al. / Thin Solid Films 517, 4593–4598, (2009).

54. Quan Zhu et al 9800 Ind. Eng. Chem. Res., Vol. 48, No. 22, (2009).

55. M. Zhang et al. / Applied Surface Science 261, 561– 566 (2012).

56. G.Y. Bae, B.G. Min, Y.G. Jeong, S.C. Lee, J.H. Jang, G.H. Koo, Journal of Colloid and Interface Science 337, 170, (2009).

57. B. Xu, Z.S. Cai, W.M. Wang, F.Y. Ge, Surface & Coatings Technology 204, 1556 (2010).

58. Harold C. Beachell, Jean C. Peterson, J Polym Sci, Part A: Polym Chem 8(7):2021-2029 (1967).

59. Chandra Mohan Srivastava, Roli Purwar, Materials Science and Engineering C, 68, 276–290, (2016).

60. Koski A, Yim K, Shivkumar S, Mater Lett, 58 (3–4):493–497 (2004).

61. Larrondo L, St. John Manley R, J Polym Sci: Polym Phys Ed, 19(6):909–920 (1981).

62. Sukigara S, Gandhi M, Ayutsede J, Micklus M, Ko F. Polymer, 44(19):5721–5727 (2003).

63. Ding B, Kim H-Y, Lee S-C, Shao C-L, Lee D-R, Park S-J, Kwag G-B, Choi K-J. J Polym Sci, Part B: Polym Phys, 40(13):1261–1268 (2002).

64. Ki CS, Baek DH, Gang KD, Lee KH, Um IC, Park YH Polymer, 46(14):5094–5102 (2005).

65. Lee JS, Choi KH, Ghim HD, Kim SS, Chun DH, Kim HY, Lyoo WS, J Appl Polym Sci, 93(4):1638–1646 (2004).

66. Zhang Y, Ouyang H, Lim CT, Ramakrishna S, Huang Z-M, 2005, J Biomed Mater Res Part B: Appl Biomater, 72B (1):156–165 (2005).

67. Roli Purwar*, K. Sai Goutham, and Chandra Mohan Srivastava, Fibers and Polymers, 17(8), 1206-1216 (2016).