TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Textile Engineering

The Study of changes in surface energy of fibre layers

Master Thesis

Study programme:	N0723A270002 Textile Engineering
Study branch:	
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	Department of Nonwovens and Nanofibrous materials

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Master Thesis Assignment Form

The Study of changes in surface energy of fibre layers

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2) Design and set materials and methods
3) Prepare fibrous materials
4) Study changes in surface energy
5) Discuss results and draw a conclusion

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1) Heng, J., et al. Methods to determinesurfaceenergiesof natural fibers :areview. CompositeInterfaces, 2007, vol. 14, p. 581–604.
2) Ferrero, F., et al. ModificationofSurfaceEnergy and Wettingof Textile Fibers. Wetting and Wettability, 201, p. 139–168.
3) Yuan, Y., et al. ContactAngle and WettingProperties. SurfaceScience Techniques, vol. 51, p. 3–34.

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Liberec November 1, 2020

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Vikash Neelakandan

Abstract

Nano-fibres are most growing and important part of textile materials as of now in this modern world. The wetting characteristics of the Nano-fibres paves way for using them in various applications mainly in the medical field. Man-made polymers are not good at wetting in their nature. Fortunately making them hydrophilic is an interesting work for implying them in numerous applications such as medical, filtration and geo-textiles applications. The surface energy of the polycaprolactone is studied in this diploma thesis. Different material parameters and process parameters are involved in this diploma thesis work for the study of the surface energy of the polycaprolactone fibre layers. Fibre layers are produced using needle electrospinning technique. The fibrous layers produced by electrospinning are tested for their surface energy using contact angle method. See System E instrument designed by Advex Instruments Czech Republic is used for calculating contact angle and surface energy of the polycaprolactone fibre layers. The results of this diploma thesis work are used for further study, and also suited for the various field application especially where the Nano-fibrous materials are used.

Key words: Polycaprolactone, Electrospinning, Nano-fibres, Wetting, Contact angle, Surface energy.

Abstrakt

Oblast nanovláken je v současném moderním světe nejvíce rostoucí a nejdůležitější odvětví textilních materiálů. Smáčení nanovláken je vlastnost, která dláždí cestu k jejich použití v různých aplikacích, zejména pak v lékařství. Syntetické polymery nejsou ve své povaze dobře smáčitelné. Naštěstí je možné je učinit hydrofilní a tím se nabízí jejich použití v mnoha aplikacích, jako je lékařství, filtrace a geotextilní aplikace. V této diplomové práci je studována povrchová energie polykaprolaktonu. Tato diplomová práce se zabývá studiem povrchové energie vrstev polykaprolaktonových vláken vlivem materiálových a procesních parametrů. Vlákenné vrstvy byly vyráběny technikou elektrostatického zvlákňování pomocí jehlové elektrody. U vyrobených vlákenných vrstev pomocí elektrostatického zvlákňování byla testována jejich povrchová energie pomocí metody měření kontaktního úhlu. Pro výpočet kontaktního úhlu a povrchové energie vlákenných vrstev polykaprolaktonových nanovláken se používá přístroj System E navržený společností Advex Instruments Czech Republic. Výsledky této diplomové práce jsou použity pro další studium a jsou vhodné také pro různé aplikace, zejména tam, kde se používají nanovlákenné materiály.

Klíčová slova: polykaprolakton, elektrostatické zvlákňování, nanovlákna, smáčení, kontaktní úhel, povrchová energie.

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1. INTRODUCTION

Textile field is one of the multilingual field as it finds importance in various fields such as geo-textiles, agro-textiles, sports textiles, Nano-textiles, automotive textiles and etc., Fibres are the basic product that were used in every day needs. The fibres are converted into products through any one of the forms namely yarns (spinning), woven textiles (weaving), webs (non-woven), composite materials. The simplest modification is done at the level of fibres. The textile products are processed in three stages mainly, pre-treatment, treatment and finishing process. For the various applications various finishes are given to the textile products. Then finishing of textile can be done in two ways. They are mechanical finishes and chemical finishes. These finishes modify the property of the fibres. The mechanical or physical finishes modify the physical property of textiles meanwhile chemical finishes modify the nature and chemical property. The modification of fibres can be done only by knowing the nature and properties of them. The Fibre layers are composed of same type of fibres or different type of fibres. The fundamental processes in textiles such as printing, dyeing and etc., needs wetting of the textiles. Wet ability of textile material in any form determines its hydrophilicity / hydrophobicity nature of them. For determination of this wet ability of textiles, knowing about the surface free energy is very important. [1]

2. ELECTRO-SPINNING

It was a long-lasting human dream to monitor the changes in the world around us and embrace those who fulfil our needs. An immense amount of progress has been made in the field of material science and development of materials with various chemistries, structures, and the properties of natural and synthetic materials, starting from small molecules and the formation of macromolecules or polymers. Subjective descriptions of nanomaterials are materials of different sizes atoms, or molecular size, up to 500 nm. Nanotechnology has had a dramatic effect development in the field of material sciences. In this thesis, Nano-fibres are produced using the electro-spinning technology. Electro-spinning technique is the majorly used for producing the nanofibers. This nanofibers structures are mostly polymeric based. The Nano-fibrous structures produced in this technique have diameter in the range between 3nm – 1000nm. As it name suggests, this spinning process uses electric field for the fibre production. In recently, the importance of electrospinning technique has been reached peak. This is due to the potential of producing a variety of polymeric fibres with a wide range of diameters in Nano scales, which is impossible in other spinning process like melt blown spinning etc., Even though melt blown technique can produce

nanofibers, large unevenness was found in the fibre diameters distribution, there is a large deviation in the diameter distribution but in electrospinning it is very small. So electrospinning is preferred for the production of nanofiber nonwoven [2]. Figure 1 shows the global market for nanofiber which increases year by year.

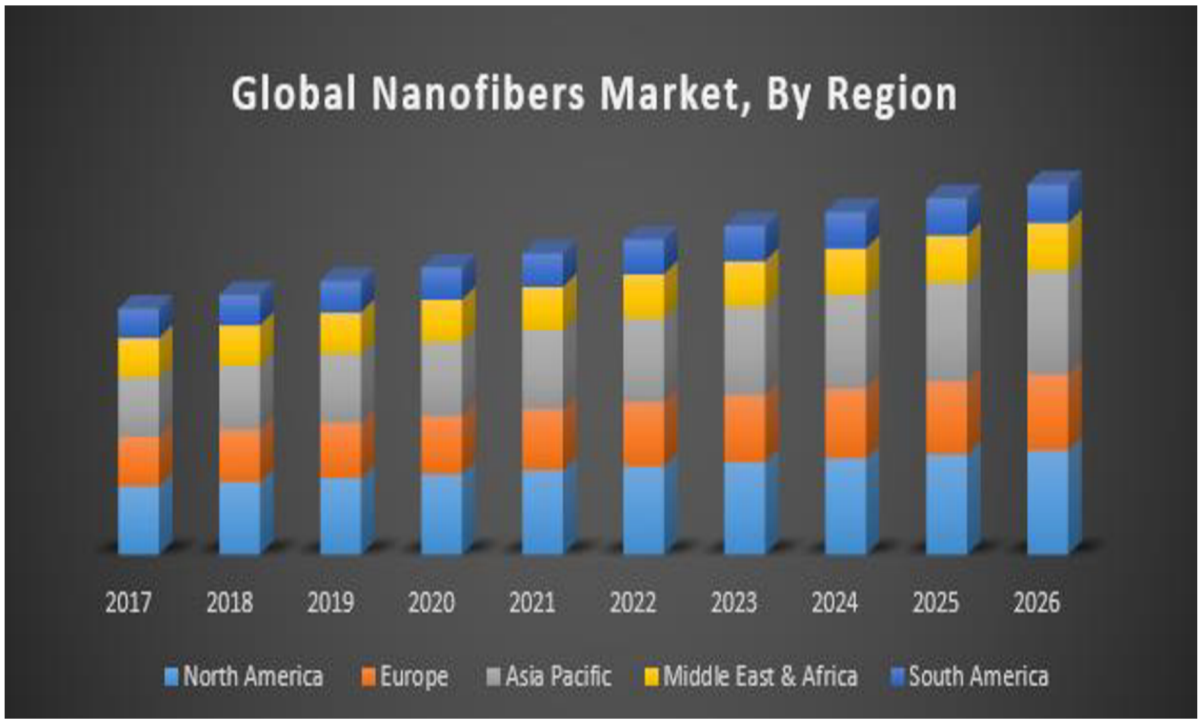

Figure 1: Graph of various region's nanofibers market till 2026 across globe [3]

2.1. PROCESS

Electrospinning process is a unique process which works with three fundamental parts. The fundamental parts are spinneret, high voltage supply and collector part. There are two types of spinnerets used in electrospinning which classifies electrospinning into two types namely needle electrospinning and needleless electrospinning process. The needleless electrospinning process is commonly used commercial process for the production of nanofibers. They use rotation cylinder in the polymeric solution or melt reservoir tank, the cylinder takes up the polymeric solution or melt during rotation and due to electric force Taylor cone was formed more than one jet on the surface of the cylinder and deposits the nanofibers in the collector. The needle electrospinning process is usually used method by the researchers in laboratory. In this method, the needle which act as the spinneret is the main part which let out the polymer solution through the nozzle. High voltage supplier is used to create potential difference between the spinneret and the collector, so that the solution gets deposited in the collector in fibre form. The collector part is may be charged

or grounded. The collector can be at any shape. The widely used collector is plate-shaped. The spinneret and collector section may be charged with same or opposite charges. Opposite polarity charges are given between the spinneret and collector where the high potential difference is required [4].

At first, the polymeric solution or melt of the polymer should be prepared. Polymeric melt is prepared by melting the polymer pellets or solid polymers by increasing the temperature above the melting point of the individual polymer. The polymeric solution is prepared by dissolving the required polymer in appropriate solvent. The dissolved viscous polymeric solution or polymeric melt is filled in syringe which acts as spinneret and the solution is injected drop by drop through controlled motor motion. The drop of viscous polymeric solution or polymeric melt that comes out from the needle nozzle in hemisphere shape. As a result of high electric forces, the hemispheric drop of polymeric solution or polymeric melt converts into a conical shape named Taylor cone. Taylor cone structure is the main parameter in this process as it results in the spinning jet. The drop in the shape of Taylor cone is driven into jet by the raising electric force at a certain value which neglects the effect of surface tension of the solution. That certain value can be termed as critical value. This jet flows in the space between the spinneret and the collector. During this jet flowing, the solution gets evaporated. This evaporation is due to the high electric force, and results in the polymer fibre production. The produced polymer nano-fibres are collected in the collector section. At last, the jet was asymmetric and follows the disturbed path caused by the interaction of many parameters such as solution viscosity, electric force, surface tension of the solution, conductivity of the solution in a complex manner [5]. Figure 2, represents the schematic diagram of basic needle electro-spinning process.

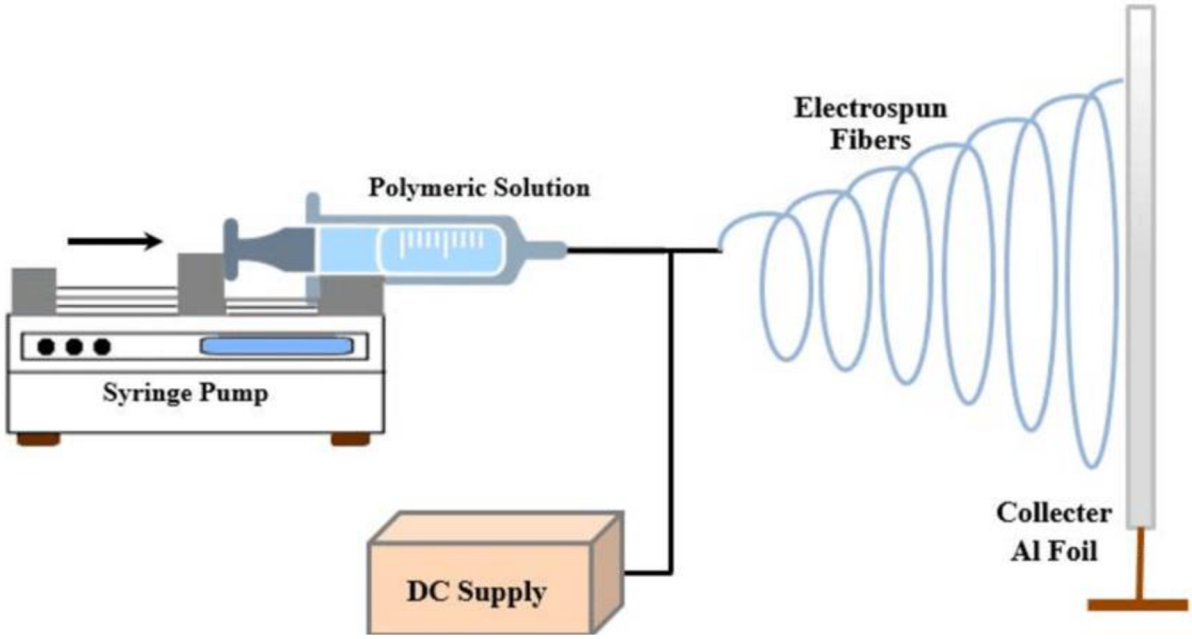

Figure 2: The schematic diagram of Needle electrospinning process [6]

2.2. ELECTRO-SPUN NANO-FIBRES

Nanofibers are produced by this technique are majorly affected by many parameters which includes the process parameter, material parameter and the environment of the production. Some of the parameters of the fibres are regulated and maintained during the production. This regulation will result in the desired quality in the produced nanofibers. The parameters of the nanofibers that should be regularly governed are:

- Diameter of the nanofiber.
- Surface of the fibrous layer
- Continuity of the fibre layer.

In the above mentioned parameters, the defect in the diameter of the fibres may result in the undesired quality of fibres such as beaded fibres, pores in the surface of the fibres. These defects in the fibres produced may affect the final properties of them. The nanofibers with the diameter in the range of Nano-meters adds up the more the advantage to this type of fibre as the ratio of surface area to volume increases. This increase in ratio of surface area to volume will lead to application in various field where the larger surface area is required. Porous, Nano-fibrous mats can be generated with a limited pore size, a wide surface area and a higher connectivity between fibres that can be used as membranes in biotechnological applications. In the same way, electrospun fibres can be designed according to their final application, all polymers with a high molecular weight can be spun

in this, with recent advances in the manufacture of natural polymer fibres, blends, etc. Thanks to this versatility of the formulations, we can make excellent components that can be integrated into the medical field, such as wound healing.

In addition to the above properties, nanofibers are often lightweight so that they can be an ideal substitute for bulky materials used as defensive textiles in biological or chemical warfare. It can act as an efficient membrane against contaminants and other biological threats, in addition to allowing soldiers to wear it for a longer period of time due to greater moisture retention and light weight [7]. Figure 3 shows the different types of fibre morphologies.

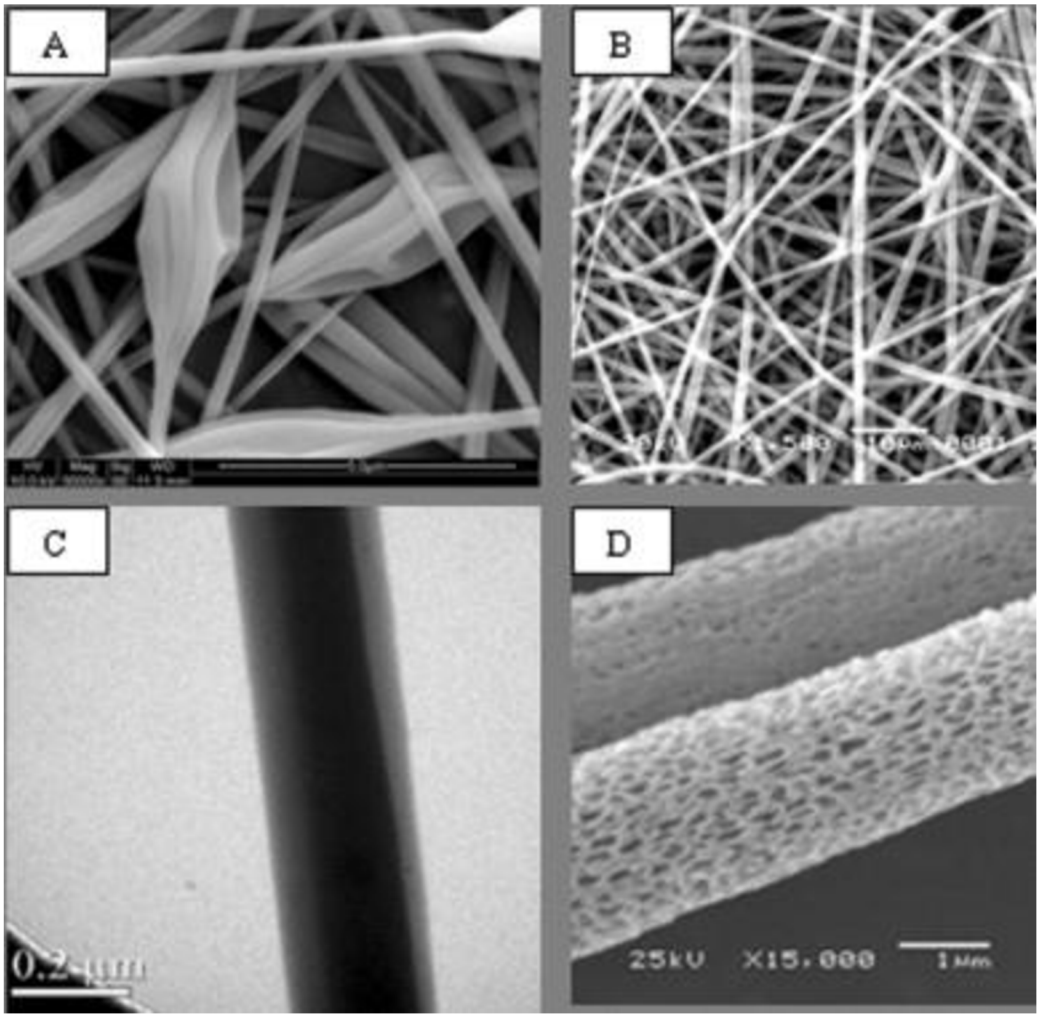

Figure 3: Types of fibre morphologies A.) Beaded fibres, B.) Soft fibres, C.) Core-shell fibres, D.) Porous fibres [8]

2.3. MODIFICATION AND IMPROVEMENT IN THE ELECTROSPINNING

Any process has its advantages and drawbacks, and so there is always the hope of changing a substance, process, parameters, apparatus or of inserting special parts into the process for a better outcome, a special product, etc. In the same way, the electrospinning adjustment can be performed in separate sections from the raw material to the collection method. These innovations are performed to monitor various aspects of the method, e.g. the orientation of fibres, the homogeneity of fibres, the amount and flow of fibres, the density of fibres, etc. Each aspect has its own field in which it is possible to regulate that particular aspect. Starting with the two important properties of the fibre, i.e. the diameter and uniformity of the fibre. Continuing with another fibre alignment property, which, if regulated, can give the commodity a proper architecture that can be useful for the electrical application of nanofiber. This property is primarily regulated by the pattern of the electrical field between the needle and the collector, which can be managed in two ways, the first is the type of collector device and the second is the different arrangement of the electrodes. The key reason behind this is to preserve a proper pattern of electrical field during the flow such that the fibre would not flow in a way that was the main drawback of the current device.

Moving further into the density of the fibres, which would similarly open up further uses for electrospun fibres. This can be regulated by the flow rate and the region at the discretion of the fibres to be processed. The key motive behind these types of setups is to limit the flow of fibres in a disorderly path (spirals of increasing diameter) that can be accomplished either by replacing the traditional needle and collector or by adding certain additional elements throughout the path to retain electrical force along the path. Electrospinning may also create long continuous yarns, but to insert twisting various equipment is added to the process, such as self-twisting or twisting two different nanofibers from two separate needles [5].

3. PARAMETERS AFFECTING THE STRUCTURE OF NANO FIBRES PRODUCED BY ELECTROSPINNING

There are many parameters in the process of electrospinning which have a major influence on the structure of the nanofiber, which may modify the different properties of the final product. And because this experiment is focused on various systems, these parameters are important to this project point of view. These parameters are either related to the machine and its surroundings or to the properties of the solution. Process parameters are voltage, flow rate, distance between collector and needle, others are the material properties such as conductivity, concentration or viscosity, solvent, and finally there are a variety of variables such as humidity and temperature that also have an effect on the substance.

3.1. APPILIED VOLTAGE

Since it has already been identified that when a high voltage induced current is supplied to a solution with the support of a needle(metal), the Taylor cone is produced after the deformation of the spherical drop and, eventually, at a critical value (varies with polymers), nanofibers are developed. When the applied voltage increases the elongated fibres and if we decrease this value below the critical value, the beads are produced in the webs, as the solvent in the fibres doesn't evaporate well. The applied voltage should then be very accurate for the standardised processing of fibres [9].

3.2. SOLUTION FLOW RATE

As same as the voltage flow rate also has a critical value that varies with the polymer system, but in some model of electrospinning machines it is not possible to change the flow rate. As the Flow rate increases, the fibres are not completely dried, thus increasing the fibre diameter and turning into beads. The minimum flow rate should be used to maintain the equilibrium between the incoming droplet and the outgoing polymer solution. Increase in the flow rate may be used to increase the thickness of the fibres, but often it may result in ribbon-like structures or fibres that have not developed.

3.3. DISTANCE BETWEEN THE NEEDLE AND COLLECTOR PLATE

The design of nanofibers can be altered by adjusting the distance between the needle and the collector, because morphology depends on variables such as deposition period, evaporation rate. It can be inferred from certain experiments that a short distance would not

cause the solvent to evaporate completely and thus the fibres have more diameter; on the other hand, the longer distance benefits the elongation of the fibres.

3.4. SOLUTION CONCENTRATION AND VISCOSITY

Nanofiber morphology depends on polymeric solution due to surface tension and viscosity. Both are governed by the concentration of the used solution. Surface tension and electrical field will break the elongated polymer chain into a low-concentration solution that will form beads. Whereas, if the concentration is high, the viscosity will also be high and so there will be further entanglement of chains which will counteract the above forces, and uniform fibres will be formed, but if there is a rise in this concentration, the beads will again develop due to the obstruction of the flow.

3.5. SOLVENT

Selection of solvents is one of the most important decisions, since certain solvent parameters, such as boiling point, surface tension, can influence the spinning of fibres and the structure of formed nanofibers. Solvents with lower boiling points are typically favoured because of their slower evaporation intensity. There would be an issue on either hand, since lower than this, it will cause dryness at the tip of the needle, thus obstructing the operation, and at a higher boiling point, non-evaporated solvents will cause beaded fibres. Another important consequence of spinning is the surface tension, since it is necessary that the solution loads resolve the surface tension for the creation of fibre, so often a combination of solvents is used to maximise various parameters.

3.6. SPINNING ENVIRONMENT

Other than the method parameter, two distinct ambient conditions often influence the fibres. Humidity affects the diameter by controlling the method of solidifying the fibres. Although the temperature regulates the evaporation rate and even the viscosity of the solution, the morphology of the Nano fibrous structure is further changed. For some of the polymers, increase in both parameters would make the surface of the fibre porous. Further raising would increase the size and width of the pores. Elevation of temperature can induce the evaporation of solvent molecules on the surface of the fibre resulting in pores on the surface. In the other side, higher humidity will cause water vapour condensation and the evaporation of both solution and water will cause porous structure [10, 11].

4.CHARACTERISTIC FEAUTURES OF NANOFIBERS

The application of Nano fibrous material is determined on the basis of its properties. These properties consist of mechanical, chemical, physical and geometric properties. As Nano fibrous materials are at the stage of growth, so many of our traditional methods of characterising them are inefficient, yet even some of them show reliable performance. We can discuss about some of the basic properties of the Nano fibrous which have impact on the end-use.

4.1. MECHANICAL PROPERTIES

It is very clear from the application of nanofiber that it has to move through several mechanical forces which can cause any deformation of the fibre, rendering it an important property. However, owing to the smaller size, it is more challenging to measure due to certain weaknesses in the handling of incredibly tiny fibres and the insensitivity of used textile machines, the observation technique which can still be carried out by Scanning Electron Microscopy (SEM), the existence of highly sensitive and precise sensors as well as actuators, and the key challenge is the processing of single stranded nanofiber. However, several successes have also been made in the development of nanofiber testing techniques that have helped to classify various nanofibers. Carbon nanotubes were measured using the Atomic Force Microscope (AFM) which used the piezoelectric principle to manipulate the fibres. The three-point bend test has been updated and can be used with fibres that can be processed by AFM anodization. Finally, a commercial nanofiber tester was developed in MTS (USA) called the Nano Bionix Device. The continuous fibre generated on a frame that is directly mounted on the machine can be easily checked [12].

4.2. PHYSICAL PROPERTIES

Many individual and essential parameters such as electrical, permeability, thermal, magnetic efficiency are included in this group (in some cases). These properties depend primarily on two distinct variables, one of which is the form of fibre and the other is the morphology of nanofiber. Former can be easily calculated from the information of the fibre base. Whereas this can be calculated by SEM and other imaging techniques. In the other hand, properties such as electrical conductivity, which can be an important property in the case of both carbon-based and metal oxide base fibres, can be studied using a digital

electrometer where the contact point has a 4mm distance between them, so that a single fibre can cross both points. Kim & Lee analysed thermal properties of certain polymer-based nanofibers and concluded that there was a small decrease in both glass transition and peak temperature crystallisation [13].

4.3. CHEMICAL PROPERTIES

The basic raw material for electrospun nanofiber is polymer, and often nanofiber has similar chemical properties as polymer. Chemical structure, bonding, molecular weight are the key properties that serve to describe the substance chemically. However, different raw materials require different parameters to define exactly as polymer-based nanofibers need replicating units and degree of polymerization, carbon-based fibre needs structural details, etc. To classify nanofibers chemically, an investigation should be done at three different levels of molecular, super molecular and surface fibre. Different techniques such as nuclear magnetic resonance and Fourier transform infrared are very useful in studying the composition of nanofiber at the molecular level. In the same way, the super molecular composition of the amorphous and crystalline regions and the orientation of the macromolecular can be determined by X-ray diffraction, optical birefringence and differential calorimeter scanning [13].

4.4. GEOMETRICAL PROPERTIES

Multiple parameters, such as fibre diameter and distribution, porosity, interconnectivity, etc., contribute to the geometric classification of Nano fibrous materials. Owing to the random process of electrospinning, a considerable amount of randomness can be used to measure geometric parameters. The diameter and distribution of fibre in Nano fibrous materials can be measured reliably using various imaging techniques. Commonly used technique was Scanning electron microscope (SEM). Due to variability, it is important to test a significant number of samples with adequate statistical assessment in order to achieve correct data. Scanning Electron Microscopy directs the high-energy electron beam on the surface of the specimen producing various signals. This produced signals help to approximate the orientation of the morphology and the composition of the specimen. Scanning Electron Microscopy produces a two-dimensional representation of the sample surface with a large magnification that can range from 20 to 30,000 times and demonstrate strong spatial variation in the specimen. Any other approaches that have been able to produce some effective outcome in the determination of these parameters. One of the

approaches is mercury porosimetry, in which we cannot keep the surface of the substance against mercury and, inevitably, the mercury can flow into the pores. The pressure exerted and the amount of mercury pushed are reported in the form of a graph, which eventually helps to measure the porosity parameters. Another of the most commonly employed techniques for the porosity and specific surface of electrospun nanofibers is the Brunauer-Emmett-Teller technique in which the adsorption of gases such as nitrogen or argon (mainly used) in an isothermal atmosphere determines the internal and individual porosity of the fibres [14].

5. APPLICATIONS OF ELECTROSPUN NANOFIBERS

From the above details, it can be inferred that nanofibers have a range of distinct properties, such as large specific surface area, small pores and their unusual ability to shape a high porosity mesh. Also, with the aid of electrospinning, we can produce fibres with both natural and synthetic polymers and with various structures that make electrospun nanofibers a very flexible product that has many applications in different fields. With the aid of constant improvements in the technology and continuing research and development of solutions, the process has been significantly streamlined with an improved production volume, which makes it an attractive commodity for both business and research purposes. Unlike other porous materials that are typically static, Nanofibers forms a porous mesh that is complex in design. These mechanisms are likely to change the size or form of the pore when some force is applied. Therefore, when combined with rigid materials, they can improve their properties and therefore nanofiber as an entity or composite material can be used for applications in areas such as healthcare, tissue engineering or biotechnology, defence or protection, environmental and energy based applications [15]. Figure 4 gives us the knowledge of application area of electrospun nanofibers.

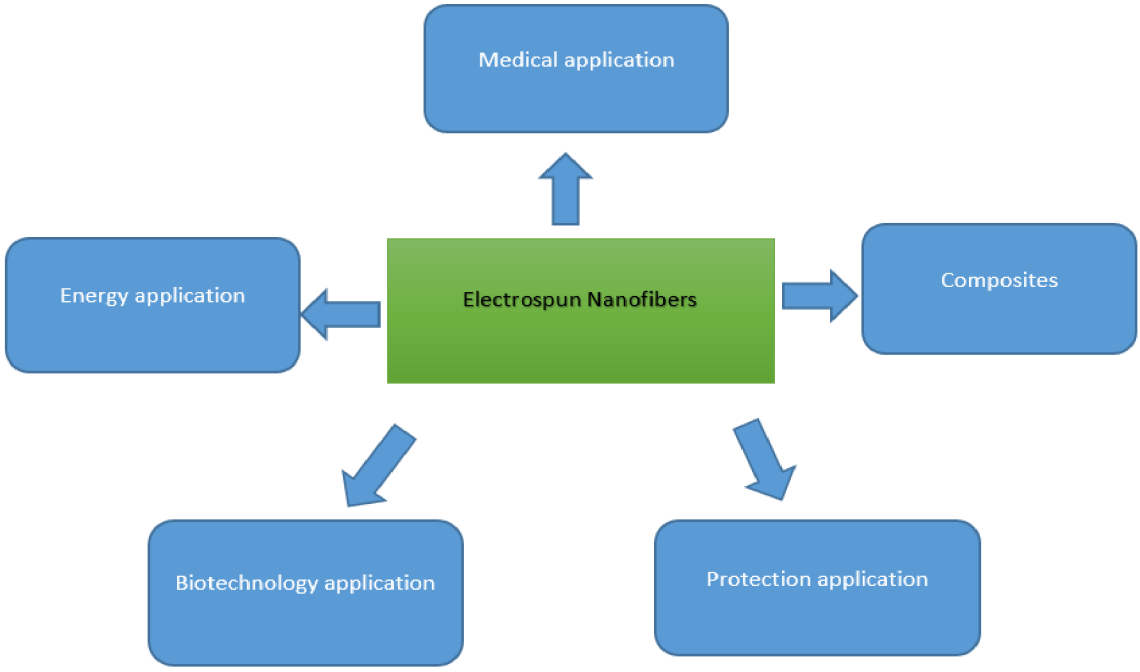

Figure 4: Application of Electrospun nanofibers in various fields. [Source: own]

5.1. MEDICAL AND HYGIENE MATERIALS

Nanofibers with their special properties have a very high ability to be used in a wide variety of applications in the area of medicine and healthcare. One of the next fields is tissue and organ restoring or regenerating tissues and implanting them within the body. The basic material used for this purpose is the scaffold on which cells are grown, multiplied and proliferated. This scaffolds can be easily constructed from nanofibers using electrospinning and phase separation. These scaffolds can be manufactured of any form or shape and proportions, their construction can be designed to offer proper cell growth and tensile properties at the same time. These scaffolds can be inserted in the body because of their biocompatibility and biodegradable properties. Other uses include a smart polymer drug delivery device in which nanofibers are used to deliver drugs to a specific region in a managed manner. These nanofibers can be used in masks for skin treatment and skin revitalization due to their adhesive and filtering properties. Biodegradable nanofiber mesh can be used as a wound dressing that forms a covering over the wound and facilitates the growth of normal skin cells, thereby reducing the healing time of the wound [16]. Figure 5, shows the various applications of electrospun nanofibers in medical field.

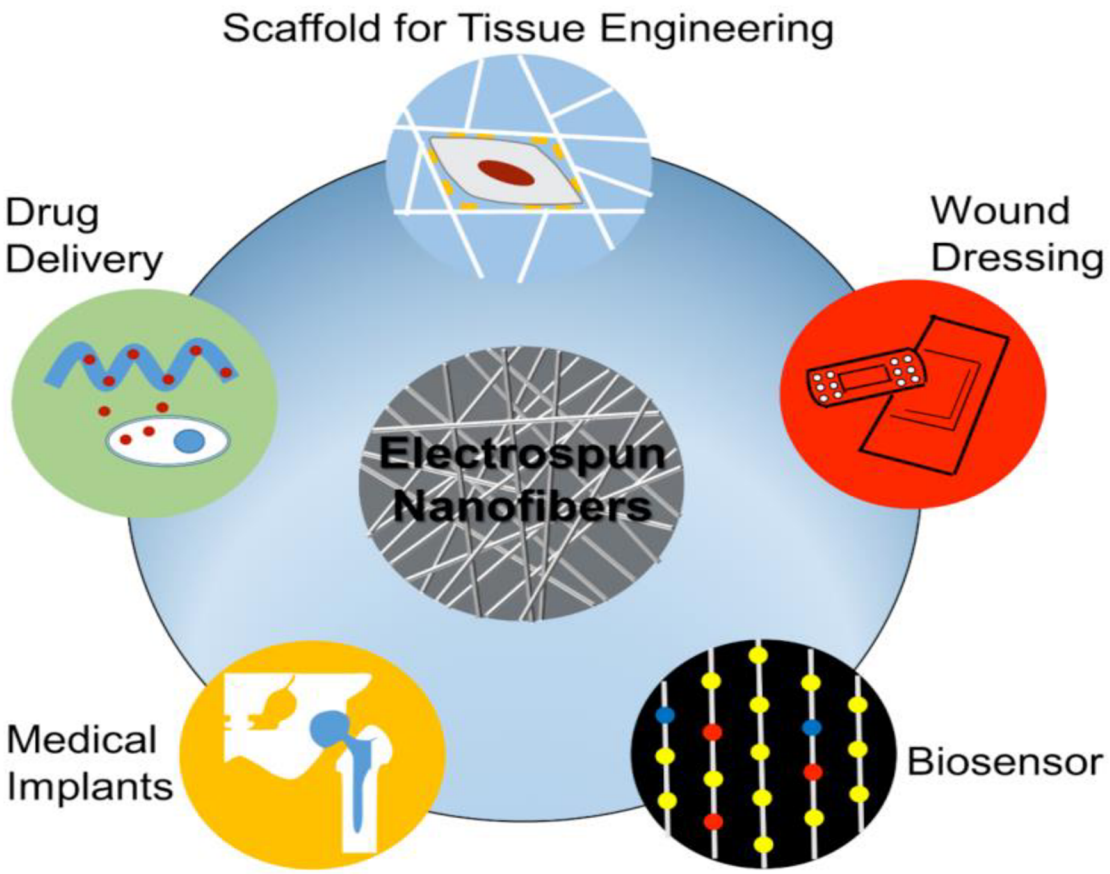

Figure 5: Scope of electrospun nanofibers in medical field [17]

5.2. COMPOSITES

With a large specific surface area and unpredictable orientation, electrospun nanofibers have a promising variety of nanocomposites to achieve stronger mechanical effects than conventional fibres, i.e. microfibers considering the lamination point of view. Due to the above mentioned properties, there would be a stronger relation with the particle of the matrices resulting in the creation of composites with superior reinforcement. There are several studies that have demonstrated the above points, in one of which the nanocomposite of Nylon showed better mechanical properties when used with epoxy. However, as far as composite theory is concerned, laminates in which fibre orientation is predetermined would provide better structural properties, and hence nanofiber consumption is lower in the composite sector [18]. Figure 6, the production procedure of composites of electrospun nanofibers with matrix.

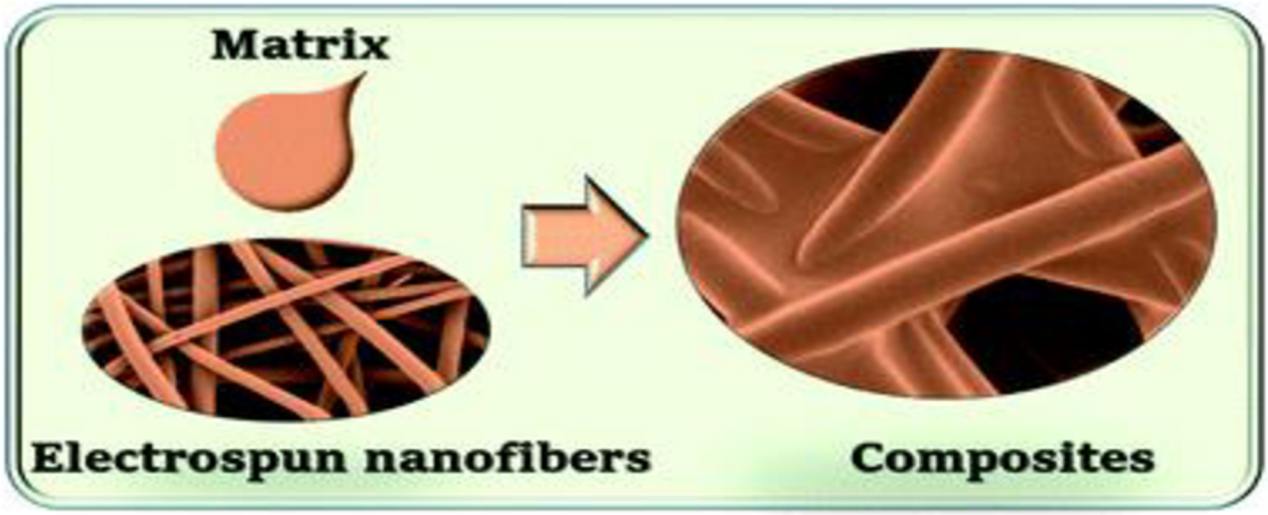

Figure 6: Schematic production procedure of composite with electrospun nanofibers [19]

5.3. PROTECTION APPLICATIONS

Nowadays, defensive gear requires a lightweight fibre with a better tolerance to all the impurities that could damage our bodies, which could be chemical or some biological infection that could harm physicians, and in case of protection we require additional properties such as ballistics. Breathability is also a very significant property that can be desired in defensive garments. As can be clearly seen from the above applications, nanofibers have been used as membranes and filters, making them very useful for all forms of medical and military protective clothing. It will shield them from biological agents of war, which will be adsorbed on the surface and killed on the surface. Face masks made up of nanofibers are widely used against chemical weapons. Membranes are changed by embedding reagents into them in a post-spinning phase that will serve as a coating in these defensive clothing [5]. Figure 7, shows the different layers of defensive clothing and the material used to make that layers.

Figure 7: Protective clothing of military soldier made up of nanofibers and other fabric [20]

5.4. BIOTECHNOLOGICAL APPLICATIONS

Membrane preparation is one of the high potential products of electrospun nanofibers due to their ability to interconnect with microscale interstitial space and high porosity with a high surface-to-volume ratio. These membranes can be used for protein purification after combination with various cells or biomolecules. These membranes have been tested as filters for airborne particles and have been found to be capable of capturing particles of less than 5µm but not less than 1µm. Further, when the liquid was tested for filtration, the membrane captured more than 95% of the particles (3-10 µm). It was also noted that most of the particles trapped were located on the surface and not between the fibres, so these membranes can be quickly collected and reused. And after the above findings, there are further applications such as water treatment that are available to these membranes [5,21]. The following figure 8 explains the production of three dimensional scaffolds which is used in biotechnology application.

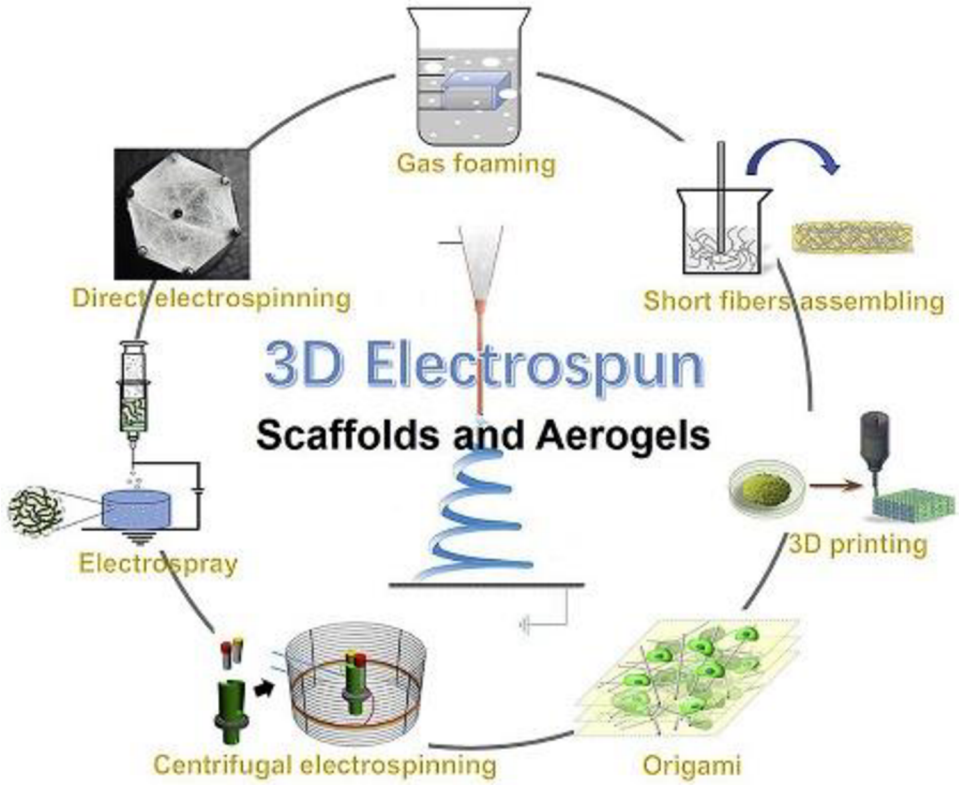

Figure 8: The schematic flow of scaffolds production with electrospun nanofibers [22]

5.5. ELECTRICAL AND ENERGY APPLICATIONS

As a result of these nanofibers, researchers have been active in reducing the size of batteries. Today, Polymer Batteries are the perfect substitute for the large lithium batteries still in operation. The polymer membrane, being extremely porous and providing a high surface area, makes it ideal for polymer batteries. The pores in the membranes allow them to retain the electrolyte liquid (water in many cases) which further facilitates the movement of electrons from anode to cathode. These batteries are currently being used on PCs, cell phones, and can be light-weighted. Nanofibers with conductive properties can be integrated into small electrical devices. Conductive nanofibers are developed by using a conductive polymer or by adding an additive with conductive properties in a polymer solution. Since it is understood that the more surface area is the electrochemical reaction, nanofibers can be used in various electronic devices such as sensors, actuators. Sensitivity is directly proportional to the surface available for sensing, so these nanofibers can be used to create an efficient sensor. Until now, several experiments have demonstrated great results in sensors used in chemical and biomedical sciences. It is often considered that if a nanofiber is manufactured using a piezoelectric polymer, it will generate a substantial piezoelectric Nano fibrous unit. Figure 9 explains the various uses of electrospun nanofibers in electrical

field [21].

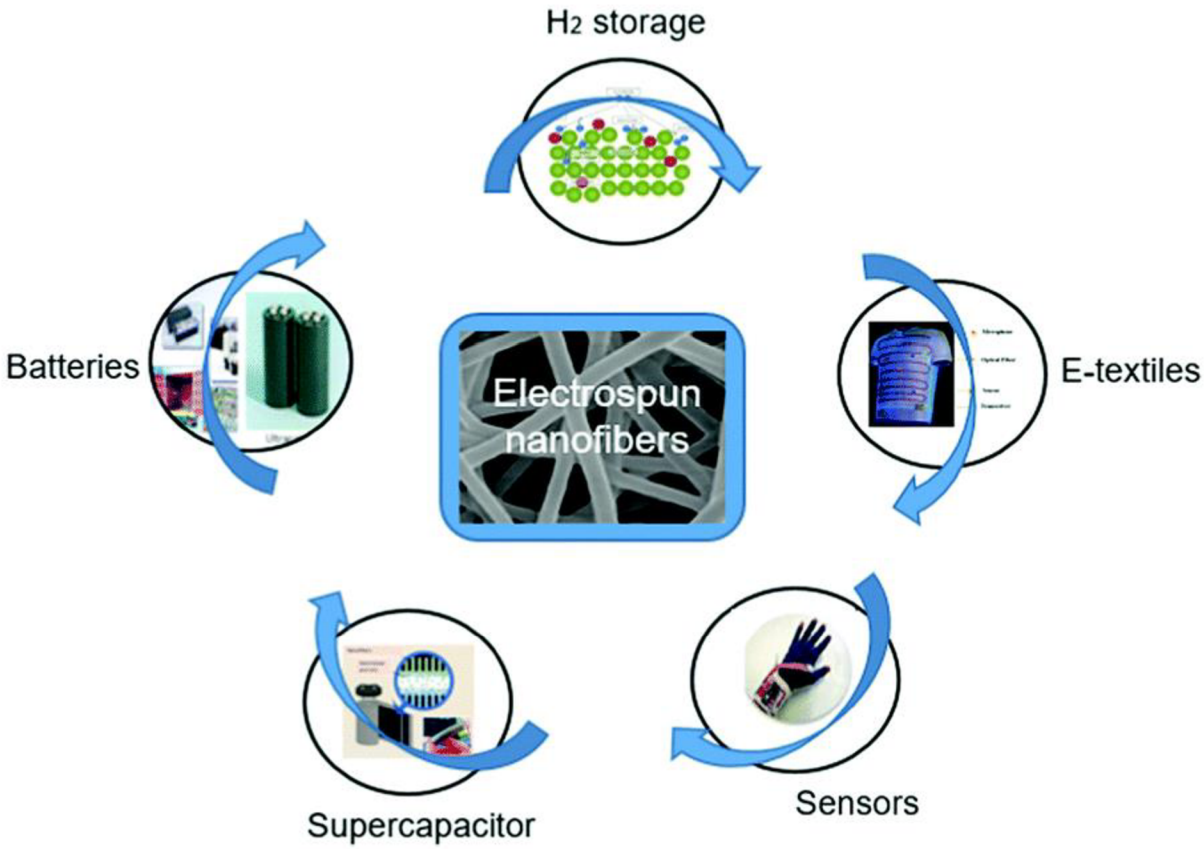

Figure 9: Electric field applications of electrospun nanofibers [23]

6. SURFACE ENERGY

In the bulk of the substance, atoms are normally stable and have a balanced series of bonds/interactions. In the other hand, the surface atoms would have an incomplete, unbalanced series of interactions and thus unrealized bonding energy. 'Surface energy' is a relative measurement of the energy at the surface. The frequency of the bulk interactions and the degree of surface exposure are positively correlated. Thus, the surface energy would be higher if the bulk interactions are larger, or if the surface exposure is higher. Surface energy would be at a higher degree if the same bulk interactions are strong and the surface emission is higher. A surface with any surface energy will often appear to reduce the energy. This tends to the adsorption of lower energy molecules on the surface of higher energy materials. Liquids quickly scatter through flat surfaces. The explanation behind this behaviour is nothing but the lower surface energy of liquids than solids. Surface energy may also be described as the energy needed per unit area to increase the size of the surface. The surface energy unit is mN/m [24]. Figure 10, shows the wetting and non-wetting nature of textile substrate.

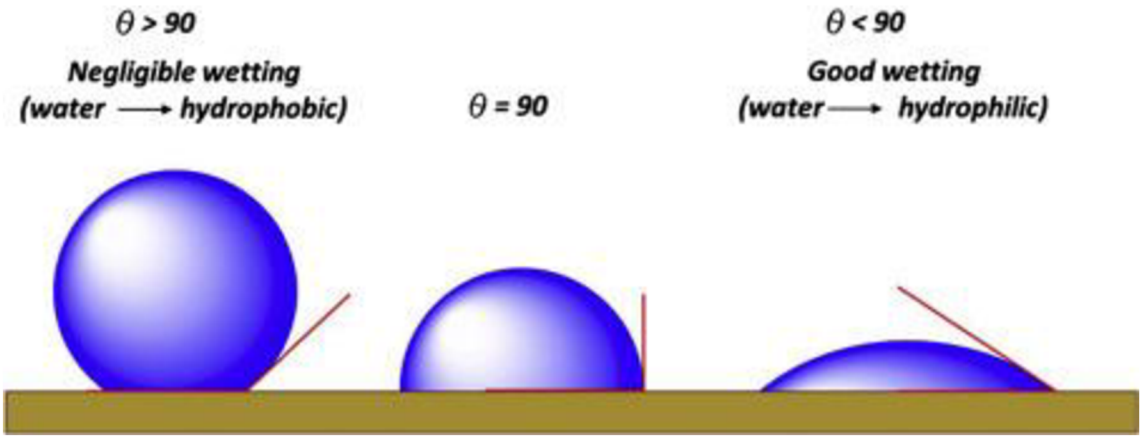

Figure 10: Explanation of hydrophobic and hydrophilic nature [25]

6.1. IMPORTANCE OF SURFACE ENERGY

The surface properties of the fibres are important factors which have an effect on the development of a textile product with certain properties. The important purpose of textile treatment is to wet textiles for painting, dyeing or some other finish. If the surface properties are not studied, there will be flaws in the handling of textiles. For example, if the fabric is dyed, any part of the fabric has low surface energy than the dye, so patchy dyeing will occur as low surface energy avoids wetting of the fabric in the dyeing solution. Surface-free energy, which allows the wetting of fibres and also provides a clear view of the adhesion between fibre layers or textile composites, is a significant surface feature to be noted. Thus, wetting of textiles is due to surface energy. In this way, surface energy is linked to the contact angle. Surface energy can be determined indirectly with the measurement of contact angle of liquid with textile layer. When measuring the contact angle and surface energy of the fibres/textiles, the surface energy of the liquid used in wetting also plays an important role [26].

Different surface energy models used	
Model name	**Used for**
Zisman	Non-polar surfaces with low surface energies
Fowkes model	Moderately polar surfaces
Owens-Wendt-Rabel & Kaelble model (OWRK)	Moderately polar surfaces
Van – Oss model	Polar surfaces (inorganic, organometallic and ionic)
Fowkes model and OWRK model	Polar and dispersive interactions of liquids
The Wu model	Good for materials with low surface energy up to 40 Mn/m
The Schultz model	Used for high energy surfaces like bare metals
The Li-Neumann equation of state	Surface energy of solid with only a single liquid of known surface tension.
Kwok-Neumann model	A greater understanding of the molecular interactions between dissimilar solid–liquid pairs has been obtained from similar pairs.

Table 1: Different models used for calculating surface energy [27]

7. MODIFICATION OF SURFACE ENERGY

Surface energy of textile fibres can be modified by various methods. By varying the surface energy of the textile materials, can obtain the result of altering the properties of them. The properties may include wetting, dyeing and printing. This modification of surface energy may also result in increasing the capacity of water and other liquids such as oil repellence. Textile materials with high surface energy will act as good hydrophilic materials and low surface energy will behave as hydrophobic material. Water is common liquid used for testing the wetting of the textile material which has surface energy of 72.8mN/m. The textile materials having polar groups gets wetted easily by the water. If the textile materials have non-polar groups or hydrophobic property, then the water poured in

them will produce spherical shape droplet on the surface [28].

Generally, fibres that are sourced from nature are mostly hydrophilic and most of the synthetic or man-made fibres are hydrophobic. But these properties were not desired always for their end application. So the modification has to be done for incorporating the desired and required properties in the selected textile fibres. As fibres are the raw materials of the textile products, modification of fibres are discussed in this chapter. Natural fibres like cotton, wool have their own unique chemical composition from nature having more hydroxyl groups. They cannot be modified to the large extent as we modify the synthetic fibre structure. As we obtain them from the nature, the environment waste, at the time of harvesting cotton the muds, and lipid layers makes them hydrophobic. So all cotton fibres should undergo pre-treatment process to make them wetting. Pre-treatment process may be done by chemical method or enzymatic method. Mainly cotton fibres are used for apparel production, so they need to be dyed or printed. For dyeing process, the fibres should be hydrophilic as most of the dyeing process is done with the help of dyeing solution. Cotton fibres are treated with alkali solution (mostly caustic soda) at hot temperature with required agents and the wastes like fats, waxes, pectin, minerals and other oils in any production methods are removed. This process also known as scouring method. Even they were given chlorination treatment making them bleached with chloride or peroxide bleaches. These scouring and bleaching makes the cotton hydrophilic and their surface was modified for this application. At recent times, the environmental pollution has been also taken in consideration and chemical scouring is gradually replaced by enzymatic scouring. The biological enzymes were developed for this purpose and applied in cotton fibres for the surface etching which modifies the surface energy and make the cotton fibre into hydrophilic. Other natural fibres like wool and silk are also done scouring for removing the waxes, vegetative wastes in their surface. In silk, there present a gummy substance called sericin, which is removed by scouring process. In other hand, chemical coating also given to make the natural fibres hydrophobic after dyeing is done. This chemical finishes can modify the surface energy of these fibres and impart the various properties that are needed.

Synthetic fibres that are originally hydrophobic and acts as water repellent materials. Due to this property they find application in manufacturing raincoats, water proof applications. Examples of synthetic fibres are polyester, polyamide and polypropylene. They have chemical structure with less polar groups, which acts as good hydrophilic agent. In same hand, they have good tensile strength and durability property when compared with natural fibres. So, they are used in many applications such as filters, composites, ropes and many

more. In some applications, the desired property is hydrophilic. But the synthetic fibres are hydrophobic. To overcome this difficulty, the surface modification has been done and the synthetic fibres are modified into hydrophilic materials. This surface modification can be done through physical methods and chemical methods. Physical methods include Plasma treatment and irradiation technique (UV) and Chemical methods done by applying post chemical treatment with finishers, oxidising agents of produced hydrophobic nonwoven materials.

7.1. METHODS OF SURFACE MODIFICATION

There are various physical and chemical methods to modify the surface of textile materials according to their end use. In this chapter we will discuss about some of the important surface modification methods of textile substrate. Physical methods of surface modification are defining as the physical modification of surface by external agents by the action of etching, irradiation, coating etc., without modifying their chemical structure. In other hand, chemical methods will modify their chemical structure at the surface and make them either hydrophobic or hydrophilic [29].

7.1.1. PLASMA TREATMENT

Plasma treatment is considered to be one of the physical methods that are used for the modification of the surface of the textile substrate. This method is mostly preferred as they are environmental friendly process. Eco-friendly process usually produces less waste and releases less chemicals so that the removing of these wastes are prevented. In this plasma treatment, no water is required and only less amount of chemicals is used. As there is no need of water, main environmental pollution of water is not done in this treatment. Whatever the modification is done on the textile substrate, the surface of them only should alter not their core properties like tensile strength, extensibility and other bulk properties. According to this statement, plasma treatment acts well in the modifications of the surface properties and alter the surface properties leaving the textile material as hydrophilic, hydrophobic according to their end use. When surface properties were modified, it facilitates wetting, dyeing, printing and other uses too. Plasma is usually known as ‘fourth state of matter’. An ionised gas made up of positive ions and free electrons in amounts that result in little to no total electric charge is known as plasma. As in this process, chemicals usage and other agents are not used in large extent, by controlling/varying the plasma variables we can obtain the good result. Plasma variables may include type of the gas used,

composition of gas used in plasma treatment, used pressure and temperature and amount of positive ions and negative ions in plasma and the time of exposing the textile substrate in plasma environment. In plasma treatment technique, there are different types of treatments such as etching, coating, cleaning and activation. Plasma surface treatment in the method of activation is considered to be replacing the textile surface polymers with the ions of plasma making the textile surface to modify into hydrophilic and hydrophobic as per requirement. In plasma activation, the non-polar surfaces of textile substrates are replaced with polar ions of plasma and make them as good lover of solvent i.e. hydrophilic surface. Usually oxygen plasma is used for this activation process. The polar ions of oxygen plasma replace the non-polar ions of surface of the textile material and make them hydrophilic. Plasma coating technique is the process of spraying the melted form of required chemicals into the surface on non-reactive textile material. This coating of this layer will make the hydrophobic surface into hydrophilic and also the vice versa product also achieved. This technique also used for deposition of metal ions on the surface of nonwoven webs. Plasma etching is the process of deterioration of surface of textile substrate with flow of plasma at speed rate and replacing the surface with ions of plasma and activating the surface of textile substrate. This process removes very little amount of bulk of textile substrate leaving them with modified surface [28, 29]. Figure 11 shows difference between plasma treated and untreated sample in hydrophilic application.

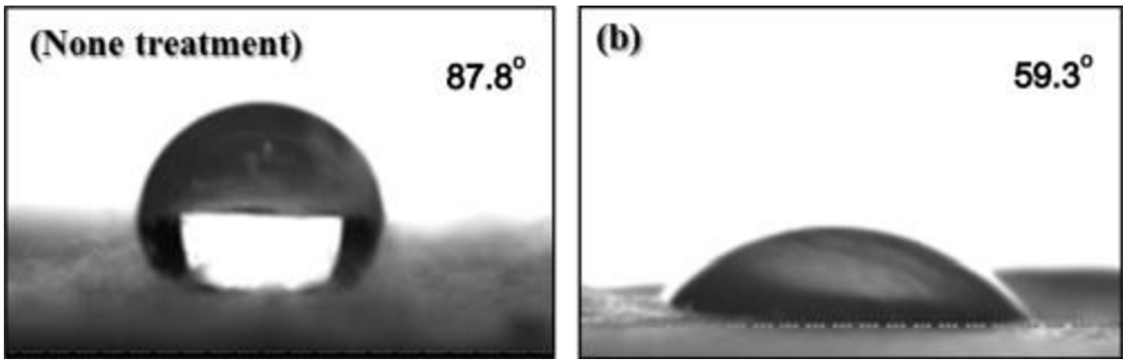

Figure 11: Water absorbency in untreated and plasma treated sample (b) [30]

7.1.2. UV CURING TECHNIQUE

As name suggests, technique is based on the exposure of textile material to the Ultra-violet rays, which modifies the surface off the exposed textile materials. This exposure will result in surface modification and helps in imparting the desired property such as wetting, water or oil repellent in the textile material. This method has advantage of modifying the textile material in only specific spot where the modification should occur, low amount of energy

was consumed, environment is polluted less compared to chemical treatment. So it can be used where localised modification is required. This technique is mostly used to impart the hydrophobic property on cotton fibres. In some of the researches, cotton nonwoven web is coated with fluoro-silicones, chitosan like chemicals to modify the cotton by increasing the hydrophobic property and antimicrobial property. After coating the mentioned chemicals, the sample is exposed to ultra-violet light. This exposure helps in cross-linking of this chemicals with the cotton structure. Through this cross-linking, the cotton surface properties are modified with the properties of these chemicals and leaving the changes in textile material. Based on the source of ultra-violet rays, time of exposure to ultra-violet rays and chemicals used, the core properties of textile substrate changes. Even the destruction of sample can also occur, if the time of exposure was high. By using this technique for crosslinking the polymers in surface. So the other side of fibre layer remains unchanged and shows the inherent property of cotton. Due to the crosslinking achieved by ultra-violet rays, the coated layer can be very thin and can be used in various application without any hindrance. This technique is recently developing technique of surface modification [31]. Below figure explains the difference in surface morphology of untreated and treated sample by Ultra-violet rays.

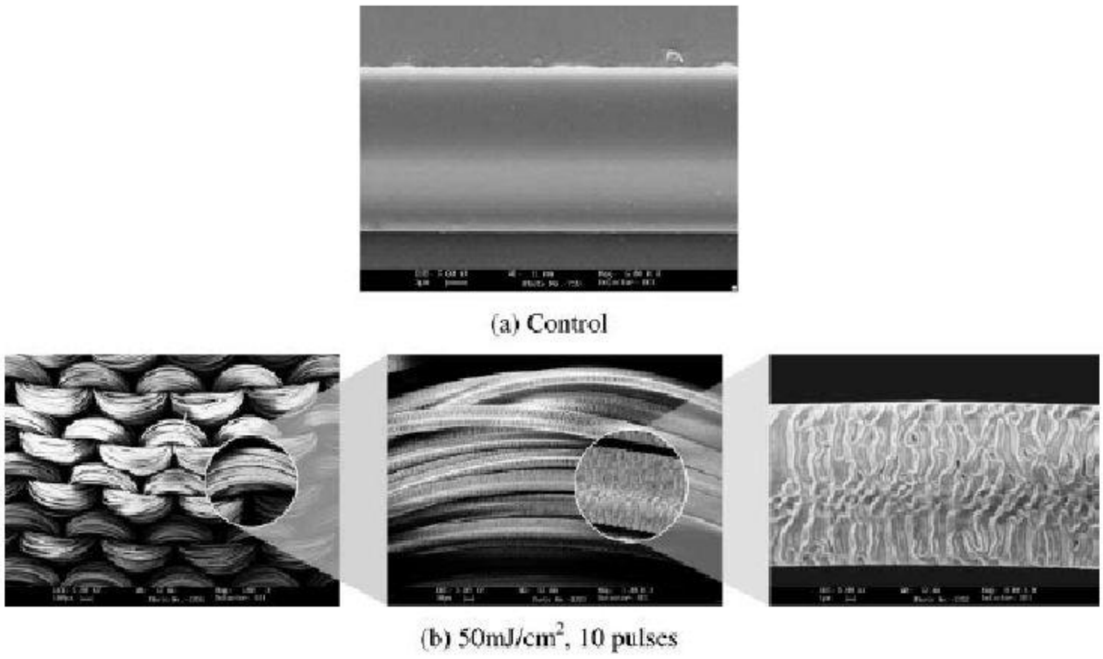

Figure 12: a) Control sample is untreated with UV, b) Treated sample with UV shows surface modification [32]

7.1.3. CHEMICAL TREATMENT

Chemical treatment is used technique for surface modification for a long time and by many industries. In this treatment, chosen chemicals are made to bond with textile surface and modify their surface property. So this technique also can be referred as chemical grafting technique as grafting of other chemicals into the fibre surface take place. As the non-polar surface of the textile substrate should be modified, the initiators are required to achieve this modification. There are various initiators which can be used as first step to make this treatment possible. These initiators are used to produce the free radicals in the surface of the textile materials, and which paves way for copolymerization of chemicals with the textile polymers. Various factors such as concentration of the used initiators, time of reaction i.e. grafting, temperature used for this process should be controlled for desired changes in the textile substrate. Recent research works gives us information like chemically treated hydrophilic fibres like cotton, viscose can be converted into hydrophobic and used in various application and also the hydrophobic fibres like polypropylene, polyester is modified and used in hydrophilic application. Some of the used initiators are potassium permanganate ($KMnO_4$), ceric ion, hydrogen peroxide (H_2O_2) etc., This treatment also used to reduce the molecular weight of polymers and increase the handling properties of them. This technique gives good result of surface modification but also creates problem regarding with environmental pollution. Due to this problem, we find an alternate method like plasma treatment, Ultra violet curing technique for the surface modification. However still this technique is in the use because of their result. Most of the functional finishes for textile goods are given through this method. The functional finished like fire resistance, water proof, oil resistance, anti-microbial properties are incorporated with textile goods through this technique [33].

8. OTHER RESEARCHES

M. M. Mirhosseini, V. Haddadi-Asl, S. Sh. Zargarian from Department of Polymer Engineering and Colour Technology, Amirkabir University have produced hydrophilic fibre layers of polycaprolactone by blending with pluronic (P123) with various proportions. They produced web with various blending proportion of polycaprolactone (PCL) and pluronic (P123) dissolved in the mixture of chloroform and methanol which is mixed in the ratio of 3:1. They produced this nanofibrous web with the help of electrospinning technique. While analysing the surface morphology of produced web with the help of Scanned Electron Microscopy images, they observed that number of beads

structure was more when PCL concentration of was low. It also observed from another angle that concentration of pluronic increases, beads structure also increases. This only concerns with number of beads. When it comes to the size of beads, it is vice versa as the concentration of pluronic increases, the size of the beads i.e. diameter of beads decreases. They tested hydrophilicity with contact angle test through drop shape analyser. This test concluded that control sample of PCL without pluronic is hydrophobic with contact angle of 132^0. But the sample they produced by blending pluronic (P123) was found to be hydrophilic. Even the small concentration of pluronic makes the PCL web hydrophilic and fits for the application of tissue engineering [34]. The following figure 13 describes the hydrophilicity of various blended samples carried out by M. M. Mirhosseini, V. Haddadi-Asl, S. Sh. Zargarian.

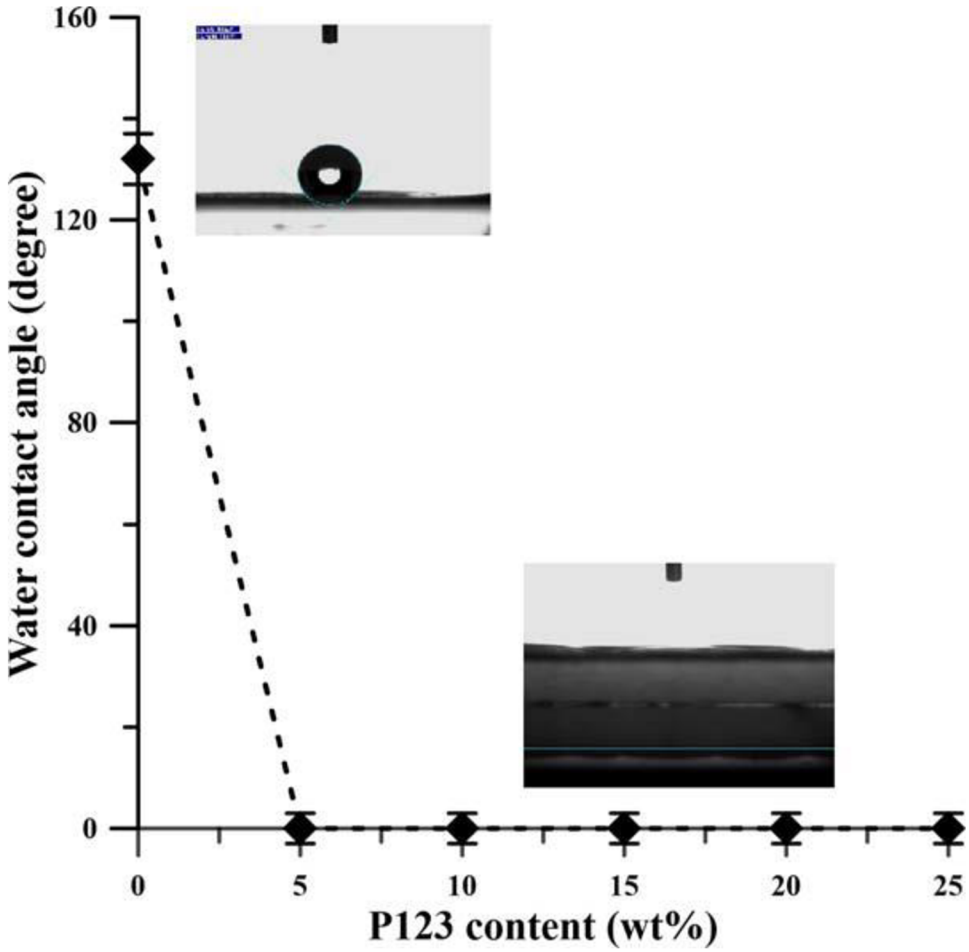

Figure 13: Different proportions of pluronic in web with their water contact angle [34]

Zahida Sultanova and other researchers from the Department of Biomedical engineering of TOBB university of Economics and Technology, Turkey had developed controlled drug delivery nanofibers with the help of coaxial electrospinning technique. They developed nanofibers with the core of polycaprolactone and ampicillin drug and shell with

polycaprolactone. They studied this technique by producing two different samples by varying the rate of flow of fluids from the coaxial needle of core and shell fluids in the electrospinning process. With this study, these researches proved that the coaxial electrospun nanofibers can be used for the application of controlled drug release. They concluded that single core electrospun nanofibers releases the drug rapidly without any control and on other hand the coaxial electrospun nanofibers made the slow release of drugs and helps in controlled release of drugs in medical textile fields [35]. The following figure 14 explains the schematic setup of coaxial electrospinning used by Zahida Sulatanova and other researches for this study.

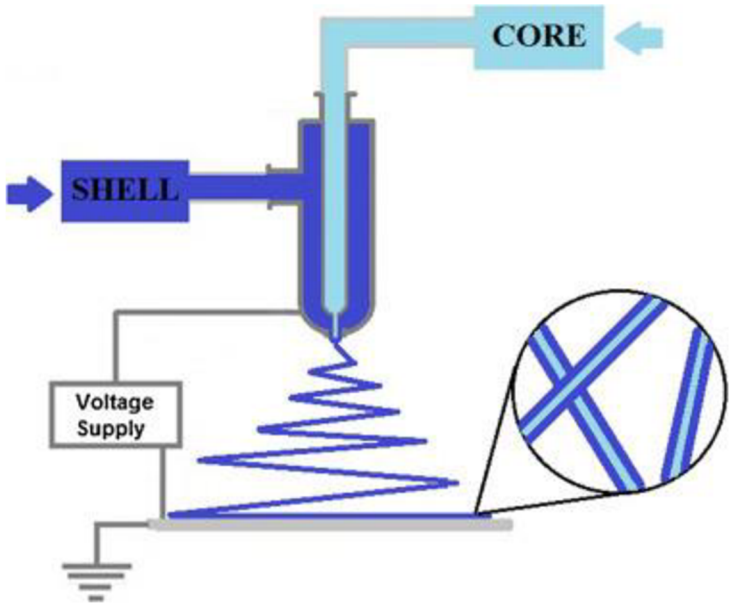

Figure 14: Schematic diagram of Coaxial Electrospinning [35]

Ipek Y Enis and his colleagues have performed a studies on alternative solvent system for polycaprolactone Nano webs through electrospinning. In this study, they used polycaprolactone at different weight percentages for producing various concentration Nano-webs. They dissolved polycaprolactone in the mixture of chloroform and ethanol in the ratio of 9:1. They also observed the changes in the physical and chemical characteristics for the polycaprolactone Nano webs by adding acetic acid and formic acid in the mixture at very low proportions. They said that adding ethanol with chloroform is to make the evaporation rate of chloroform to slow up which will impact in good spinnability of polycaprolactone. They also proposed that average fibre diameter of fibres produced from polycaprolactone with chloroform and ethanol solution through electrospinning increases as concentration of polycaprolactone increases. Addition of acetic acid and formic acid results in decreasing of fibre diameter which is used to produce Nano-scale

fibres through electrospinning. This research group has concluded that the reduction in fibre diameter may be due to the increase in the conductivity of the polymeric solution which is given by adding formic acid and the reduction in surface tension of electrospun web by the addition of acetic acid. They also given a point that there is no change in the viscosity of polymeric solution by adding acetic acid and formic acid. This study conveys the point that electrospun webs of polycaprolactone with chloroform and ethanol can be produced by adding acetic acid and formic acid, which can be used in the area of tissue engineering for further development [36].

Ismail Tiyek and other researches with him investigated the hydrophilicity of polycaprolactone electrospun Nano-webs by altering the process parameters of electrospinning. They found that by varying the process and material parameters, hydrophilicity of polycaprolactone webs were increased. They made the polycaprolactone pellets to dissolve in two different solvent mixtures. One of them were chloroform and ethanol in the ratio of 9:1 and other solvent mixture was chloroform and dimethylformamide in the ratio of 9:1. They also studied the physical and hydrophilicity characteristics by varying weight concentration of polycaprolactone used to form electrospun web. In this study, they used needle electrospinning process for the production of electrospun web. Kruss tensiometer were used for measuring the surface tension of the polymeric solutions. They found that the process parameters like high-voltage and material parameters like viscosity and concentration majorly affect the surface characteristics of produced web. They studied and recorded that high concentration of polycaprolactone will have high wetting which was found to be the result from low contact angle. Also, they stated that using low voltage during electrospinning will produce more beads structure and results in low wetting. They performed this study and came to conclusion that 18% of weight concentration of polycaprolactone with two solvent mixtures found to be hydrophilic when they are electrospun at the voltage range of 20-25 kV [37]. The following figure 15 shows the Scanned Electron Microscopy image of the samples produced by Ismail Tiyek and other researchers at different voltage.

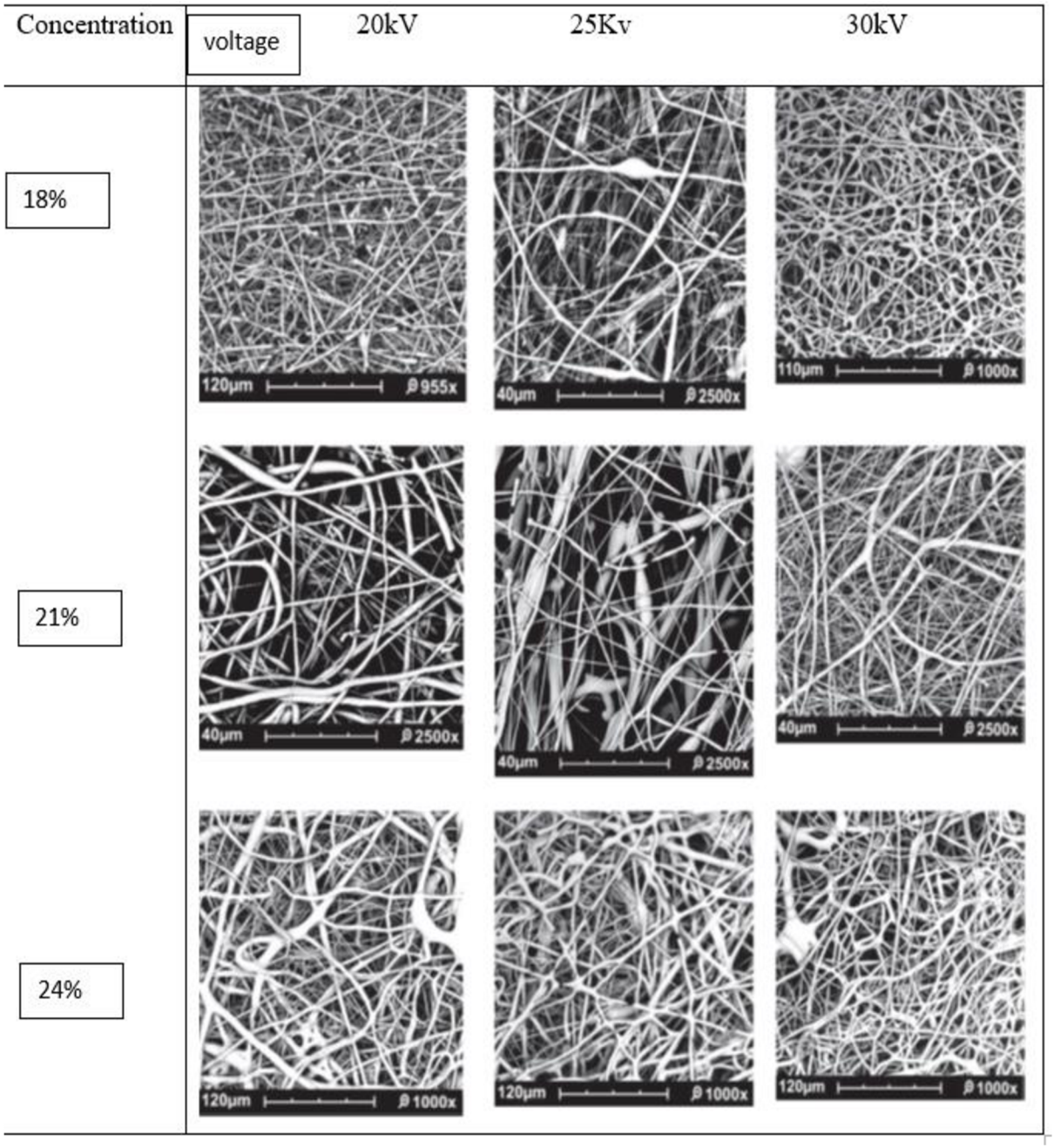

Figure 15: Scanned Electron Microscopy images of samples at different given voltage [37]

9. CHEMICALS USED

In all thesis work, chemicals play a vital role same as the instruments and technology used. Although there are many chemicals we use some of them for this study of surface energy of polycaprolactone fibrous layers. In this chapter we discuss about the nature, physical properties and chemical properties of the chemicals that has been used in this thesis work.

9.1. POLYCAPROLACTONE

Polycaprolactone is a polymer made up of monomers unit of hexanoate. It is sub divided in the aliphatic polyesters class. IUPAC name of the polycaprolactone is poly(hexane-6-lactone). The chemical representation i.e. chemical formula for polycaprolactone is $(C_6H_{10}O_2)_n$. Common method of production of polycaprolactone is done by using ε-caprolactone as monomer and processed by the process of ring opening polymerisation method. In this synthesis process, metallic or ionic catalyser is used. Other synthesis process includes the radical ring opening polymerisation method of 2-methylene-1,3-dioxepane and the method of condensation of 6-hydroxycaproic acid. Polycaprolactone is chosen among wide range of polymers as their applications are very vast. Figure 16 shows the chemical structure of polycaprolactone. [38]

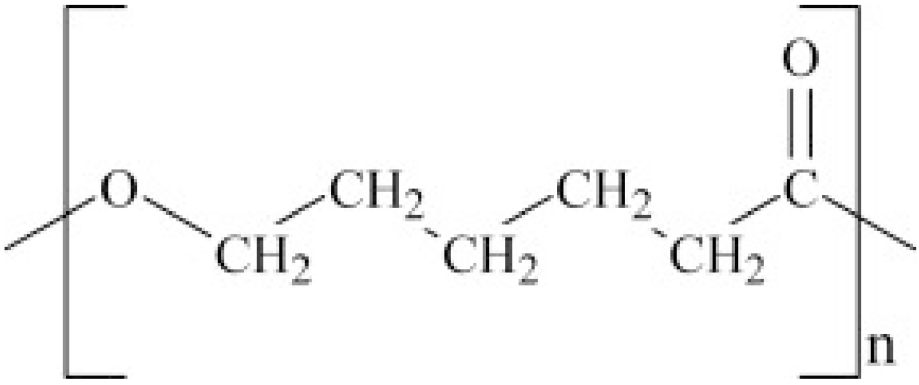

Figure 16: Structure of Polycaprolactone. [39]

The physical properties of polycaprolactone such as biodegradability, biocompatibility paves way for the usage of this polymer in the field of medical and tissue engineering. Polycaprolactone is mostly used in the research in the field of drug delivery systems. They are commonly investigated for blending with different polymers and copolymers. This polymer also commonly used in the manufacturing of special types of polyurethane which is employed in implantable bone tissues. This type of polymers is used in rapid prototyping technique which uses 3-dimensional printing procedure for the production of many types of human tissues and organs as emerging technique. Polycaprolactone also used with

natural polymer such as starch to reduce the cost of the product made by them and also to develop the degree of biodegradability of the product. Polyvinyl chloride (PVC) blended with polycaprolactone so that polycaprolactone can be used as plasticizer. Polycaprolactone used in drug delivery systems and tissue engineering for producing different implants which requires high biocompatibility and biodegradability. In chemical view point of polycaprolactone, they can be used for the purpose of additives for the material called resin. This additive polycaprolactone improves the processing ability of resin and also their final applications such as impact resistance etc., The physical properties of polycaprolactone such as density of common polycaprolactone is 1.145g/cm^3, melting temperature (T_m) of polycaprolactone is 60^{0}C, glass transition temperature (T_g) of polycaprolactone is -60^{0}C. Polycaprolactone is hydrophobic polymer by nature but it can be made hydrophilic by further finishing treatments like physical methods such as ultra violet radiation, chemical treatments like using oxidising agent or other chemicals, enzymatic treatments etc., [38,40] Applications of polycaprolactone in various fields is shown in the figure 17.

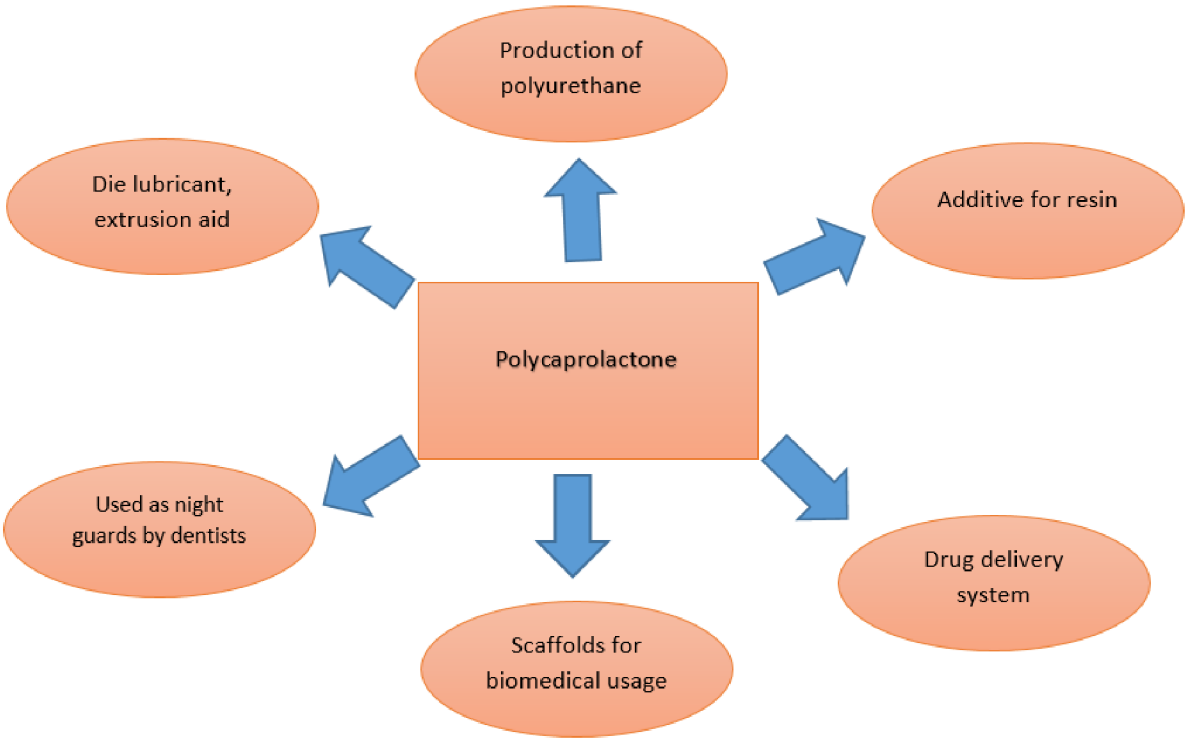

Figure 17: Applications of Polycaprolactone in diverse fields. [Source: own]

9.2. CHLOROFORM

Polycaprolactone is dissolved in selected solvents to make polymer solution for electrospinning. Chloroform is most optimised solvent system for polycaprolactone in older researches. Chloroform is the colourless liquid which is mostly used as solvents, reagents, anaesthetic agent and also for criminal cases. IUPAC name of chloroform is trichloromethane, which is chemically represented i.e. chemical formula by $CHCl_3$. Figure 18 shows us the chemical structure of chloroform. Density of chloroform will be in the range between $1.4 g/cm^3$ – $1.55 g/cm^3$. The chloroform consists of hydrogen which is attached with carbon will take part in hydrogen bonding with the solute particles. Here the solute particles are polycaprolactone. [41]

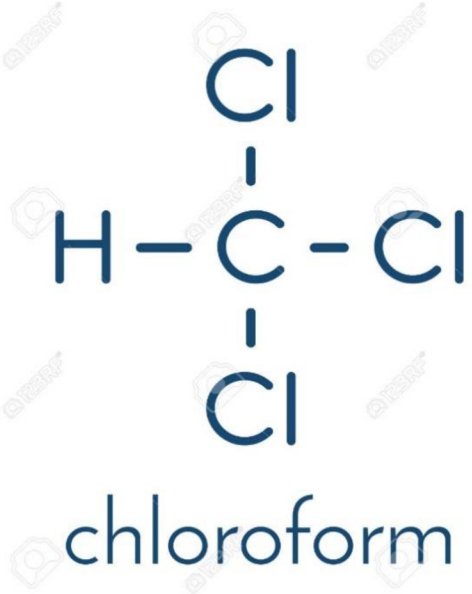

Figure 18: Chemical Structure of chloroform. [42]

9.3. ETHANOL

Ethanol is also added in solvent system. Ethanol is from the alcohol family and also known as the ethyl alcohol. It is represented by the chemical formula of C_2H_5OH. The chemical structure of ethanol is represented in the figure 19. It is the type of alcohol that is mostly consumable with further processing and also used as reagents, solvents. It is used in the solvent system for improved spin ability of polycaprolactone which is electrospun using needle electro spinning technology. [43] Ethanol also helps in reducing the evaporation rate of chloroform which results in better spin ability of polycaprolactone as explained above in the research work of Ipek Y Enis.

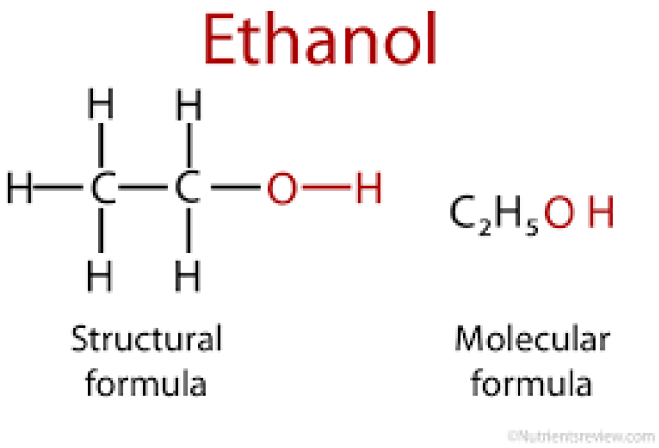

Figure 19: Chemical Structure of ethanol. [44]

9.4. ACIDS

Acetic acid and Formic acid also used as solvent system in proper ratio. Acetic acid and Formic acid solvent system is selected for the result of reduced fibre diameter which will be in the range of nanometres. Formic acid is the simplest carboxylic acid and colourless acid. It is also known as methanoic acid. It has pungent smell. It is found naturally in ants. Formic acid is used in many biological industries like livestock feed industry, poultry etc., It is represented by chemical formula of HCOOH. Acetic acid is the second most fundamental carboxylic acid. It is also called as ethanoic acid. It is represented by the chemical formula of CH_3COOH. It is used as industrial chemical, reagents in different sectors, in medical field and also used as food in processed form. [45,46] Chemical structure of acetic acid and formic acid is shown in figure 20.

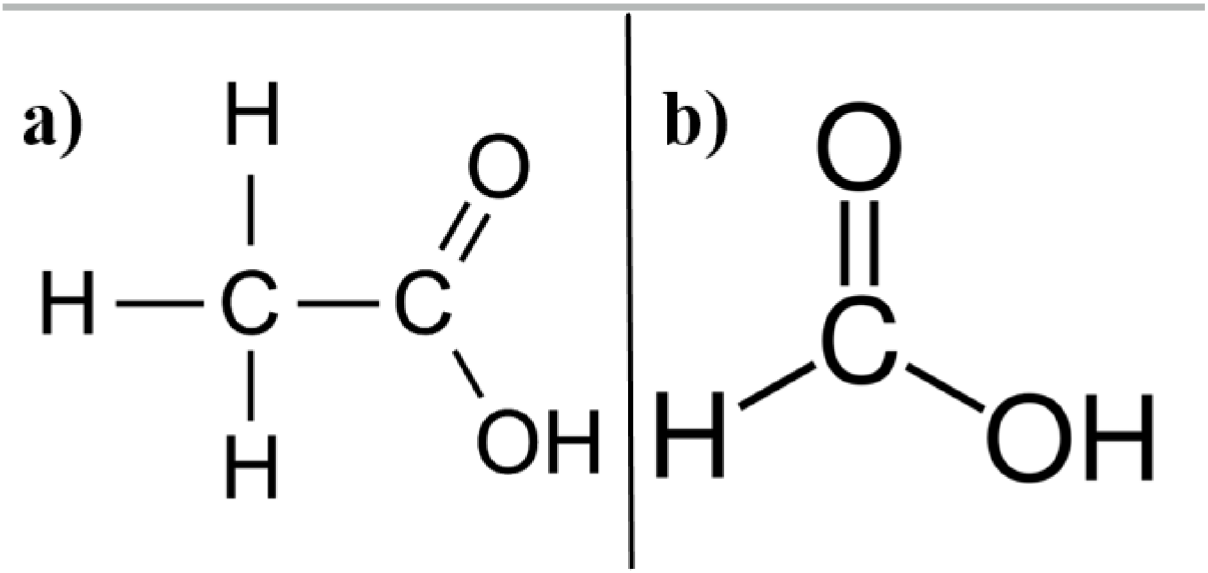

Figure 20: a) Chemical Structure of acetic acid [47] b) Chemical Structure of formic acid. [48]

9.4. ACETONE

Acetone, which is the simplest form ketone is used in one of the solvent systems used in this experiment. Acetone is also called as propanone, which is colourless, flammable and highly volatile liquid. It is represented by the chemical formula of $(CH_3)_2CO$. Figure 21 represents the chemical structure of acetone. It can be mixed with water, so it serves as important organic solvent in research labs, chemical industries and also in medical labs. [49]

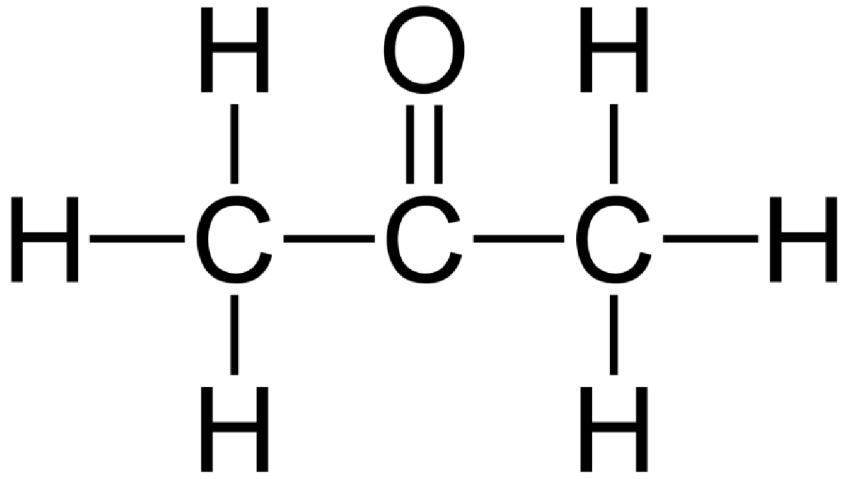

Figure 21: Chemical Structure of Acetone. [50]

9.5. GLYCEROL

Glycerol is the chosen liquid for this experiment. Usually water is used for wetting the formed web. Glycerol is one of the simplest polyol chemical compounds. Glycerol is made up of triol structure. It has base structure of propane in which hydroxyl groups are sub suited at the certain places. IUPAC name of glycerol is represented as propane 1,2,3-triol. Glycerol is mainly seen as naturally occurring chemical. They are seen in stomach of human and it makes the water to stay in the gut which helps is digestion of food. They are mostly derived from human beings and animals in the form of triglycerides and esters of glycerol with acids (long-chain carboxylic acids). From this precursors, glycerol is obtained by the chemical reactions such as hydrolysis, saponification and also trans-esterification. This reactions result glycerol with fatty acids as sub products. Glycerol are commonly colourless liquid. Glycerol are also can be miscible with water. Their boiling point is around 290^0C. They also exhibit odourless and also tastes sweet. They are viscous liquid and non-toxic chemicals as they are mostly naturally occurring compound. The physical structure of glycerol consists of backbone chain of proteins namely glycerides. On

the account of this protein presence, they are also used as medicines in treating wound and flame burns of human skin. They are also used as natural sweetening agent in food processing industry. Glycerol also find its application in the field of chemical industries as chemical intermediate, also as vibration damping fill in pressure gauge due to their viscosity. They also used in the refilling liquids of electronic cigarettes, which are available in various flavours. They also used as an antifreeze agent in older days. [51,52,53] The chemical structure of the glycerol is represented by the figure 21 given below.

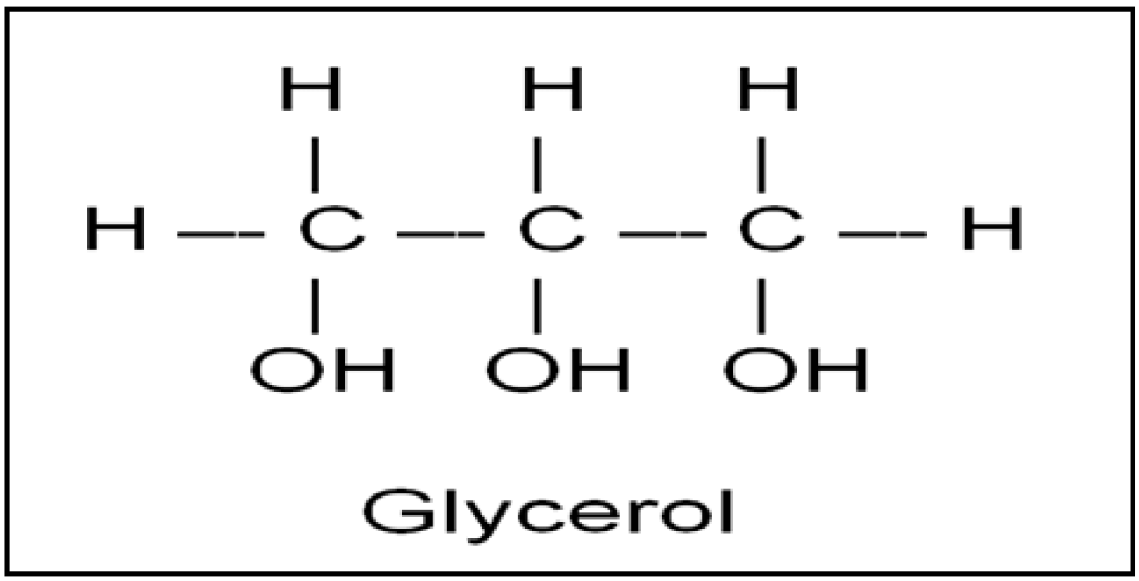

Figure 22: Chemical Structure of glycerol. [54]

10. EXPERIMENTAL PART

10.1. GENERAL

This experimental part of the thesis will explain on the basis of theoretical plan of preparing non-woven web and testing it for wetting characteristics. This wetting characteristics of the polymer non-woven web will pave way for numerous applications. The theoretical plan for producing web and testing for their wetting characteristics is discussed in this chapter. The experimental part of the thesis mainly devoted to the production of polymer based nonwoven and testing of their characteristics of wetting by contact angle method. This thesis is mainly depending on the increasing of hydrophilic characteristics of Polycaprolactone by modifying the parameters of the production of their web. The plan of this experiment is represented in the form of flow chart in the figure 22.

10.2. OBJECTIVE

- Selection of material and method
- Preparation of polymer web
- Testing of their wetting characteristics

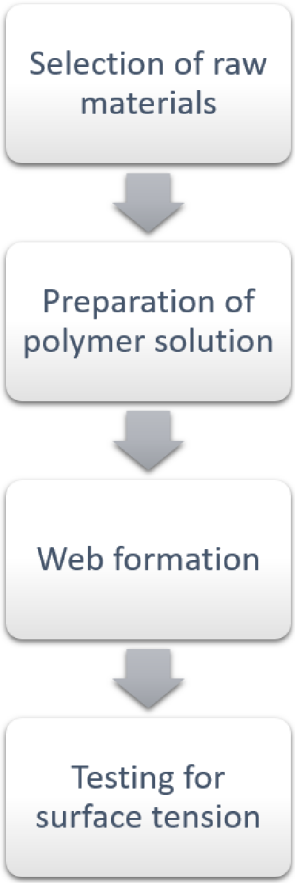

Figure 23: Flow chart of experimental work of thesis. [Source: Own]

10.3. MATERIAL AND METHODS

In this chapter, the raw material required for the formation of polymer web and also other raw materials required for this experiment is discussed. Also the method of preparing solution of polymer and the method of web formation is discussed here in this topic.

10.3.1. SELECTION OF RAW MATERIALS

Selection of fibre or polymer is the first and foremost step in the manufacturing of the web. As per the requirement of end process, the raw material is chosen from wide range of fibres or polymers. In development research, new fibres or polymers are selected as raw material and processed and tested for their required characters. This clearly tells us how important is the selection of raw materials which has immense impact in the final properties of the end

product. In this experiment, polycaprolactone polymer is chosen for testing their wetting characteristics. Polycaprolactone of molecular weight of 45000Mn. Polycaprolactone used are in the form of pellets.

In this thesis, we use three types of solvent systems in which polycaprolactone is dissolved for the purpose of electrospinning. Each solvent systems are prepared perfectly with proper ratios as described below.

Solvent System 1:

Used Chemicals	Chloroform	Ethanol	Acetic Acid
Ratio (in parts)	8	1	1

Table 2: Chemicals used in solvent system 1. [Source: Own]

Solvent System 2:

Used Chemicals	Chloroform	Ethanol
Ratio (in parts)	8	2

Table 3: Chemicals used in solvent system 2. [Source: Own]

Solvent System 3:

Used Chemicals	Formic Acid	Acetone	Acetic Acid
Ratio (in parts)	1	1	1

Table 4: Chemicals used in solvent system 3. [Source: Own]

10.3.2. PREPARATION OF POLYMER SOLUTION

Preparation of polymer solution depends on the concentration of polycaprolactone to be spun into web. All raw materials are calculated with proper weighing machine according to the requirement. Polymer polycaprolactone is available in pellets which has molecular mass of 45000Mn. They are weighted according to the concentration. As polycaprolactone is biodegradable we should prepare fresh polymer solution for web formation through electrospinning. 40gram of polymer solution is prepared at a time and used for the web formation through electrospinning. When 40gram of polymer solution is prepared, the weight of the polycaprolactone is first taken according to the concentration to be used. Then we will calculate the solvent chemicals based on the solvent system used to prepare polymer solution. Polycaprolactone and solvent chemicals are taken in closed conical flask. Conical flask is placed in magnetic stirrer. With the help of magnetic stirrer, the polymer

polycaprolactone and the solvent system is stirred for minimum of 12 hours. After the sufficient stirring, the polymer solution for the web formation through electrospinning is prepared.

Calculation of polymer solution:

40gram of 16% of polycaprolactone polymer solution is prepared through solvent system 1.

Chemicals	Weight taken in grams
Polycaprolactone	6.4
Chloroform	26.88
Ethanol	3.36
Acetic acid	3.36

Table 5: Weight calculation involved in preparation of polymer solution 1. [Source: Own]

40gram of 18% of polycaprolactone polymer solution is prepared through solvent system 1.

Chemicals	Weight taken in grams
Polycaprolactone	7.2
Chloroform	26.24
Ethanol	3.28
Acetic acid	3.28

Table 6: Weight calculation involved in preparation of polymer solution 2. [Source: Own]

40gram of 14% of polycaprolactone polymer solution is prepared through solvent system 1.

Chemicals	Weight taken in grams
Polycaprolactone	5.6
Chloroform	27.52
Ethanol	3.44
Acetic acid	3.44

Table 7: Weight calculation involved in preparation of polymer solution 3. [Source: Own]

40gram of 16% of polycaprolactone polymer solution is prepared through solvent system 2.

Chemicals	Weight taken in grams
Polycaprolactone	6.4
Chloroform	26.88
Ethanol	6.72

Table 8: Weight calculation involved in preparation of polymer solution 4. [Source: Own]

40gram of 18% of polycaprolactone polymer solution is prepared through solvent system 2.

Chemicals	Weight taken in grams
Polycaprolactone	7.2
Chloroform	26.24
Ethanol	6.56

Table 9: Weight calculation involved in preparation of polymer solution 5. [Source: Own]

40gram of 14% of polycaprolactone polymer solution is prepared through solvent system 2.

Chemicals	Weight taken in grams
Polycaprolactone	5.6
Chloroform	27.52
Ethanol	6.88

Table 10: Weight calculation involved in preparation of polymer solution 6. [Source: Own]

40gram of 16% of polycaprolactone polymer solution is prepared through solvent system 3.

Chemicals	Weight taken in grams
Polycaprolactone	6.4
Acetic Acid	11.2
Formic Acid	11.2
Acetone	11.2

Table 11: Weight calculation involved in preparation of polymer solution 7. [Source: Own]

40gram of 18% of polycaprolactone polymer solution is prepared through solvent system 3.

Chemicals	Weight taken in grams
Polycaprolactone	7.2
Acetic Acid	10.93
Formic Acid	10.93
Acetone	10.93

Table 12: Weight calculation involved in preparation of polymer solution 8. [Source: Own]

40gram of 14% of polycaprolactone polymer solution is prepared through solvent system 3.

Chemicals	Weight taken in grams
Polycaprolactone	5.6
Acetic Acid	11.47
Formic Acid	11.47
Acetone	11.47

Table 13: Weight calculation involved in preparation of polymer solution 9. [Source: Own]

10.3.3. WEB FORMATION

The next step of this thesis is formation of web with the polymer solution prepared. As discussed above, production of nanofibers is usually achieved through the technique of electrospinning. There are two types of electrospinning, one is needleless electrospinning and other is needle electrospinning. Needleless electrospinning is commonly known for industrial use for bulk production. As this thesis is experimented in laboratory, needle electrospinning technology is the best choice. Needle electrospinning setup consists of a spinneret, collector and voltage producer. Needle is the spinneret of this electrospinning technique. Prepared polymer solution of polycaprolactone is taken in the syringe, which acts as needle in the laboratory setup of electrospinning. As said before, this experiment has its main focus in altering the process parameters and material parameters of electrospun polycaprolactone and test them for the hydrophilic characteristics. As discussed in the literature part, the parameters that affects the electrospinning process are:

(i) Applied voltage.

(ii) Solution flow rate.

(iii) Distance between the spinneret and the collector.

(iv) Spinning environment.

(v) Diameter of the needle.

In this experiment, two parameters are altered and the web of polycaprolactone is formed. Applied voltage and the needle diameter is altered and other factors like solution flow rate, distance between the spinneret and the collector, spinning environment are kept constant. Polymer solution od polycaprolactone prepared in different concentration are loaded in the needle which acts as spinneret. The polymer solution flow rate is kept constant at the value of 3.0milliliter per hour for this experiment. Spinning environment were kept constant, as whole of the experiment was planned to perform in same lab and same electrospinning machine. So the environment of the electrospinning was constant for all the samples. This constant factors will help in deciding the parameters which has effect on the physiological characters of the web produced. The distance between the spinneret i.e. needle and the collector is kept constant and it was measured around 12 centimetres. Voltage applied on this experiment and the diameter of the needle used for this experiment are used with different values and different diameters respectively and studied the physiological changes in the web. Voltage applied will have adverse effect on the formation of web as it makes polymer solution to spin and even giving high voltage than the optimum level will also lead to the negative effects on the web. In the case of diameter of the needle used, varying the diameter will lead to the visible changes in the physiological characteristics of the web. Variations of the voltage given to the web formation is shown below in the table 14:

Name of the sample	Voltage applied
Type 1	12 kilovolts
Type 2	15 kilovolts
Type 3	20 kilovolts

Table 14: Variations in the applied voltage for this experiment. [Source: Own]

Different diameter needles that are used in the web formation is given below in the table 15:

Name of the sample	Diameter of the needle used
Type 1	0.45 mm
Type 2	0.80 mm
Type 3	1.10 mm
Type 4	1.20 mm

Table 15: Variations in the needle diameter used in this experiment. [Source: Own]

10.4. ANALYSIS OF FORMED WEB

Web of polymer polycaprolactone formed by the electrospinning technique with individual solvent system and varying process and material parameters is taken and analysed. First, the web produced from various variations are taken and analysed for the physical appearance and fibre orientation through the instrument called Scanning Electron Microscope usually denoted as SEM analysis. This SEM analysis will help us to understand the surface of the fibre layers, which has impact on the wetting. SEM analysis should be carried out carefully, as they involve maintaining the testing environment. Usually for the SEM analysis, samples were mounted on aluminium stubs and sputter-coated with gold to a 10-20 mm thickness. Morphological analysis or Physical appearance analysis can be done at various places of the fibre sample. By testing at various places on the sample will help in better understanding about the fibre distribution and orientation of the fibre layer. With this analysis, we can understand the orientation which will show some impact during wetting stage of fibre layer of polymer polycaprolactone formed through the technique called electrospinning technology.

10.5. WETTING OF FORMED WEB

As the thesis works under the topic of surface energy of fibre layers, finding surface energy of different fibre layers formed by varying parameters is essential. For the calculation of surface energy in this thesis, System E instrument is used. This instrument use contact angle method for the calculation of surface energy of fibre layers. The major part of contact angle method of analysing surface energy of fibre layers is wetting of it. Wetting is the essential step to be carried out for the contact angle analysis. Glycerol is the liquid used for wetting the formed fibrous layer. A drop of glycerol is dropped on the surface of the fibrous layer of polycaprolactone produced by the technology of electrospinning. This wetting of the fibrous layer can be carried out at different places of the fibrous web for the accuracy of the calculation. Micro pipette can be used for wetting the formed polycaprolactone fibrous web.

10.6. TESTING FOR SURFACE ENERGY

After wetting of the fibrous web of the polymer polycaprolactone, determination of contact angle of glycerol with them is carried out. With the help of contact angle of glycerol formed with the polycaprolactone fibrous web, surface energy of fibre layers of polycaprolactone can be calculated. For the determination of contact and surface energy of polycaprolactone fibrous layer, an instrument named SEE SYSTEM E can be used. The instrument called See System E is manufactured by Advex Instruments, Czech Republic. This instrument has an ability to calculate both the contact angle and surface energy of the sample provided. A sample image of See System E is given below in the figure 23.

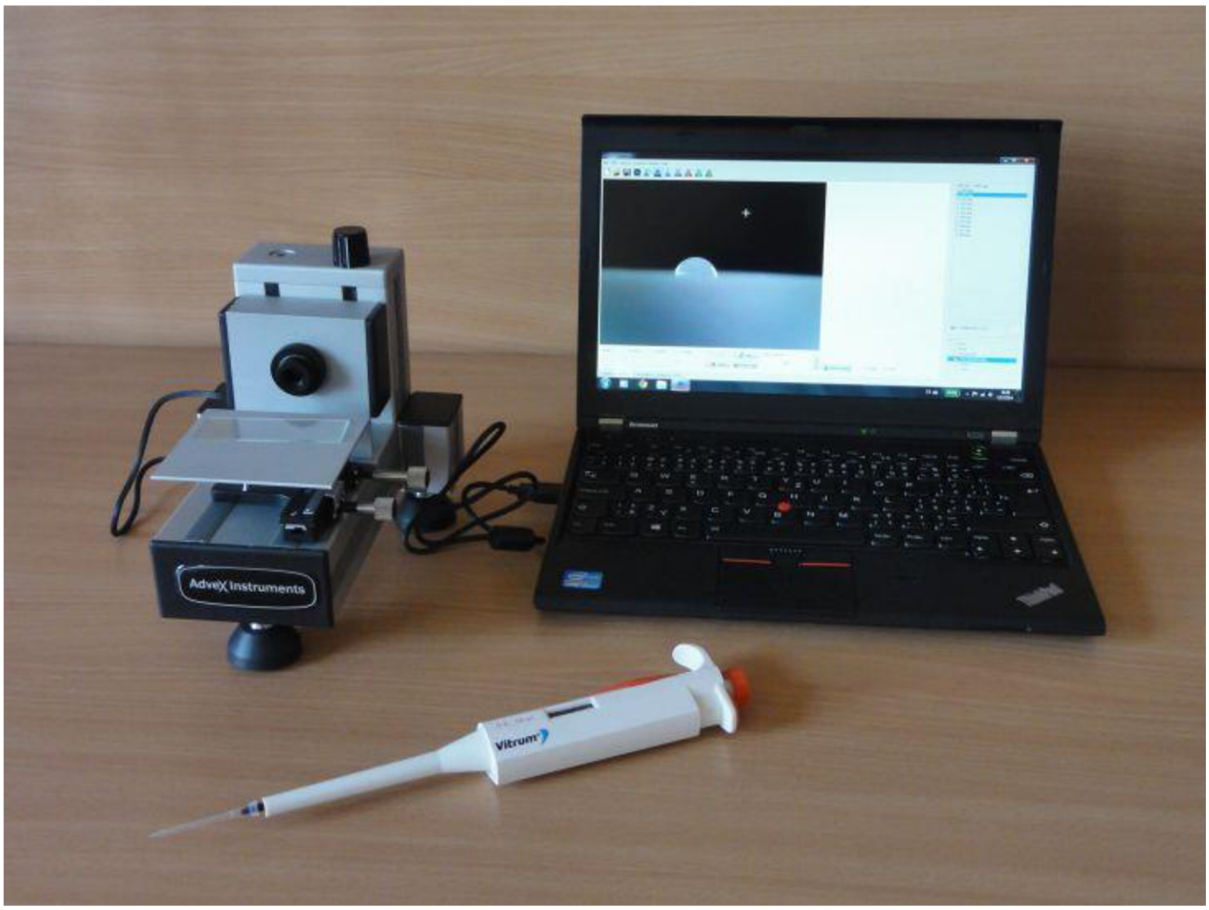

Figure 24: Example of See System E instrument designed by Advex Instruments, Czech Republic. [55]

See system E is an instrument which is very handy and easily transportable and portable. Due to this portable design, they can be used and accessed in various locations wherever the researchers moves and carried out his/her experiment. This instrument has Universal Serial Bus (USB) connectivity with the computer. This connection cable helps to connect with the computer in various lab. This manufacturer also offers See System E software

which can be installed in computer to which this instrument is connected for testing and measuring of the contact angle and surface energy. This software developed by the Advex Instruments helps us to calculate the surface energy through various surface energy models namely, Owens-Wendt-Rable-Kaeble, Lifshitz-van der Waals/acid-base, Li-Neumann, Kwok-Neumann, Wu Equation of State, Zisman. Here in this thesis, we use kwok-neumann model for the determination of surface energy of fibrous layers of polycaprolactone. This instrument consists of image capturing unit which is colour 2 Megapixel USB Video Class (UVC) camera. This camera unit is facilitated with high resolution glass objective lens. This instrument also has a sample placing stand on which the sample with dimension up to 10cm x 10cm can be placed and tested for surface energy of the samples. As this instrument holds camera of good quality, external light source is not needed for performing the experiment. Normal daylight is far enough for the capturing the wetting stage of fibrous layer of polycaprolactone. This image captured by See System E is used for the determination of contact angle. With the determined contact angle from the captured image, the surface energy of the fibrous layer of polycaprolactone is derived by the kwok-neumann method. This See System E instrument designed by Advex instruments also facilitates the periodic imaging technique which was very useful in analysis the time dependent wetting of the web by the glycerol liquid. As this instrument facilitates the big sample size testing, we can test the fibrous layer of polycaprolactone in different places by wetting them. The testing for surface energy can be calculated for all the samples prepared with different proportions of solvents. When the sample is placed in sample plate and wetted with the glycerol liquid with the help of micropipette, the image capturing unit i.e., camera captures the glycerol interaction with the fibrous layer. This image of interaction of glycerol with the fibrous layer of polycaprolactone gives us the information on contact angle. With this contact angle, surface energy is calculated automatically by the software designed by the Advex instrument. Result of this test is displayed in the computer which is connected with See System E instrument through USB port. Result consists of data of contact angle of interaction and surface energy of the fibrous layer of polycaprolactone. [55] Working of this See System E instrument is explained in the figure below.

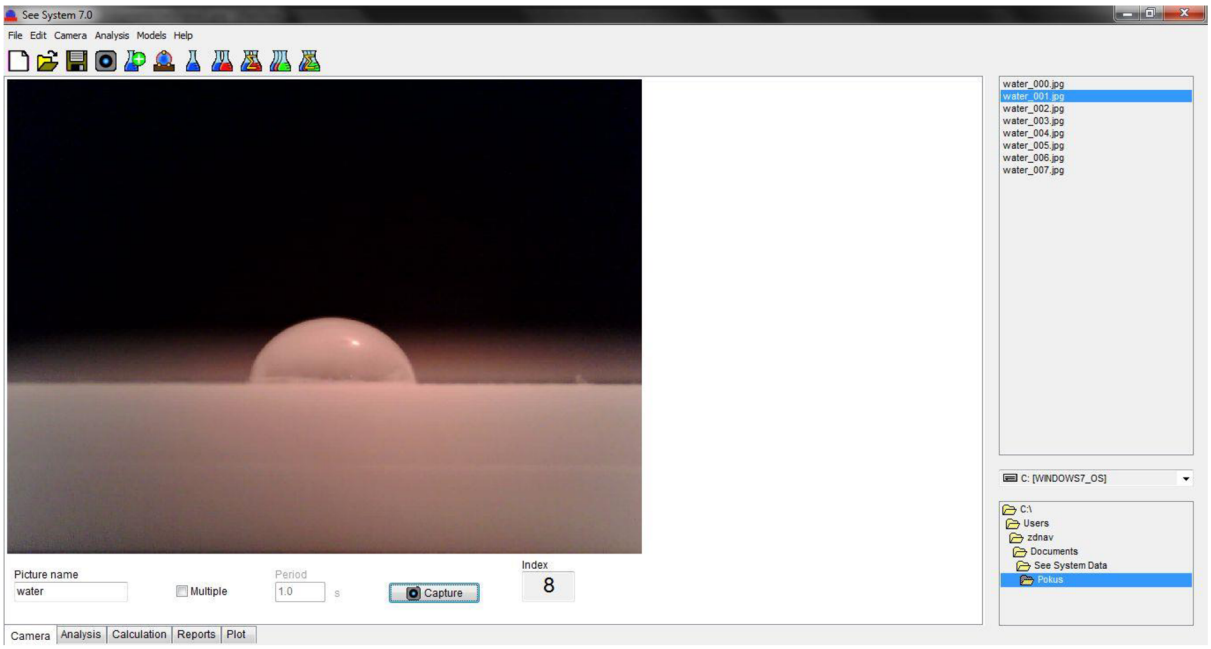

Figure 25: Step 1 – Capturing the interaction of liquid with sample. [55]

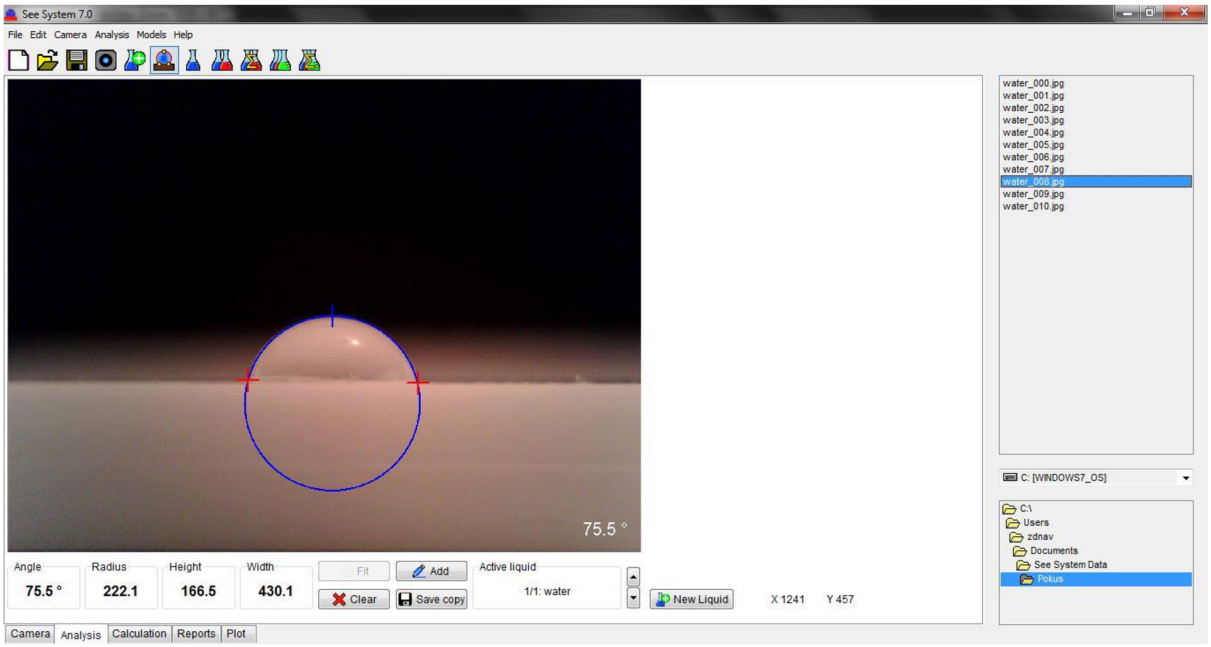

Figure 26: Step 2 – Marking the bubble for calculating contact of angle. [55]

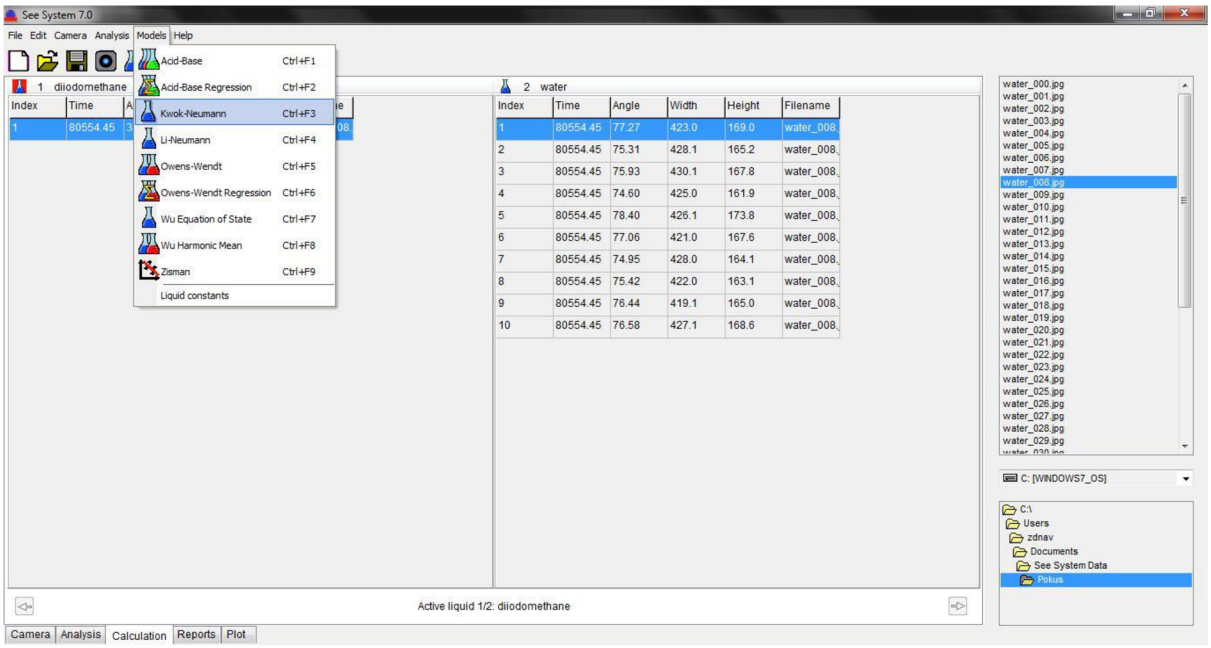

Figure 27: Step 3 - Selecting the surface energy system for calculation of it. [55]

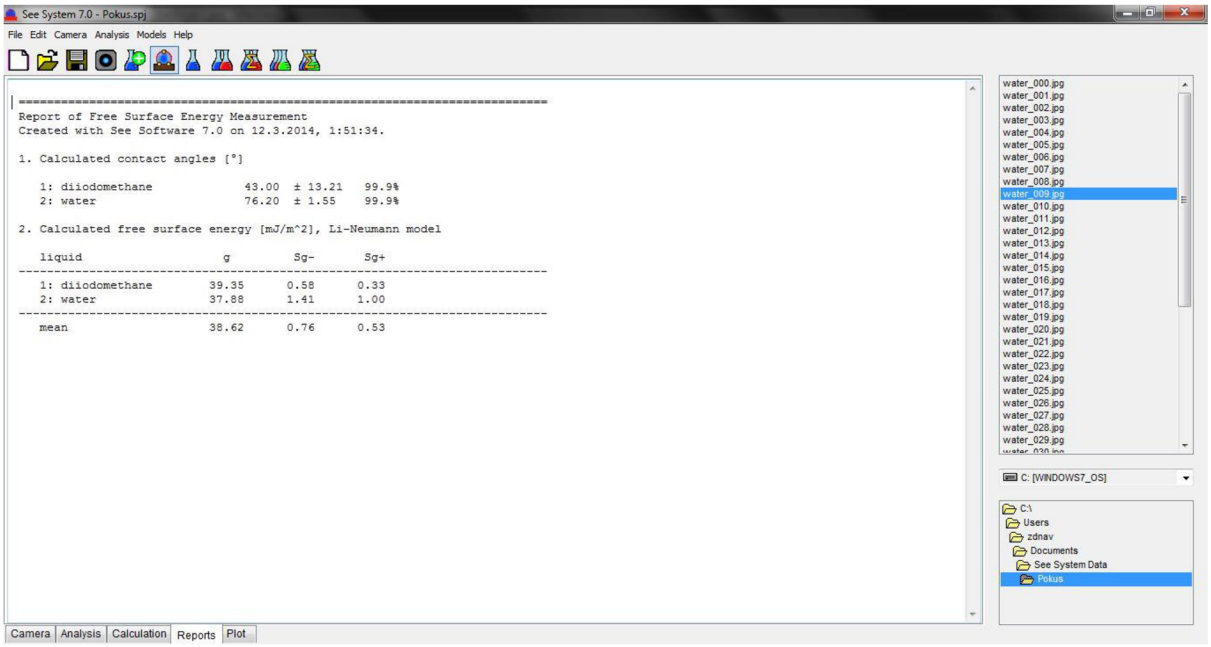

Figure 28: Step 4 - Displaying the calculated contact angle and surface energy. [55]

11. RESULT AND DISCUSSION

According to this study, by preparing polymer solution of polycaprolactone with different solvents, forming web through electrospinning technique and tested for their surface energy values with help of See System E, the hydrophobic polycaprolactone can be modified into hydrophilic without any surface modification. By varying the process parameters, the result of hydrophilic polycaprolactone is achieved. By testing the produced samples, result is expected to be low contact angles is measured for the high concentration of polycaprolactone samples. 18% of polycaprolactone samples will show the low contact angle, which implies high wetting when compared with low concentration of polycaprolactone samples i.e. 16% of polycaprolactone sample will show lower wetting and higher contact angle than 18% of polycaprolactone sample and 14% of polycaprolactone sample will show lower wetting and higher contact angle than 16% of polycaprolactone. When we compare the used voltage variations for the study of wetting, usage of low voltage i.e. 12 kilovolts will result in high beaded structure when compare with higher voltage used. This high beaded structure will result in high rough surface structure which induce hydrophobicity. So the sample of polycaprolactone web produced using 20 kilovolts will result in high wetting which is resulted from low contact angle reading from See System E. In diameter variations, needle with small diameter gives uniform fibre layer. As needle i.e. spinneret of electrospinning has impact on the fibre orientation. We use 0.45mm diameter needle, which is smallest among the needles we use for this study. The sample with this diameter needle gives more uniform fibre orientation. This uniform orientation fibre layer of polycaprolactone which is result of 0.45mm diameter needle will result in high wetting when compared with other samples produced from other diameter needles. This study gave the understanding that polycaprolactone can be made hydrophilicity with varying only the material and process parameters instead of any surface pre-treatment or post treatment.

12. CONCLUSION

As we discussed in previous chapters, the polymer polycaprolactone is used in various applications. When the polycaprolactone is selected for any application, the key point for the selection is its low cost and degradability. Although, polycaprolactone is hydrophobic polymer, it is used in various applications where hydrophilicity is required by doing surface modifications. This study will help in developing the hydrophilic polycaprolactone web without any surface modifications. This development leads to replacement of costlier hydrophilic polymers by the polycaprolactone. When the low cost, degradability and hydrophilic properties are put together, this polymer becomes huge useful. Nowadays, natural cellulose fibres possesses the properties like degradability and hydrophilicity. This development of hydrophilicity polycaprolactone will make a big change over in industrial textiles. Even though, hydrophilic polycaprolactone is available now with the chemical surface treatments, polycaprolactone fibre layer produced by varying parameters will have a big opening for the industrial field. This surface treatment given to polycaprolactone will add upon the cost of them. So this study paves a way for handling this problem and gives us a much required solution. Development of this type of hydrophilicity polycaprolactone polymer may be used in wound care of medical textiles, automobiles and also in various technical textiles field.

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