



Fabrication of Various Nanofibrous Hybrid Membranes for Separation of Micro-Particles

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Institute of Mechatronics and Computer Engineering





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Abstract

As evidenced by growing scientific and industrial research in recent years, nanofiber membranes created by electrospinning engineering are being committed to novel applications for developing technologies. Membranes are highly successful because of their characteristics, which include a small pore size, a vast specific surface area, and the excellent filtration. This nanofibrous filter is the most fascinating study in the previous decade due to availability of nanofiber raw materials and particular useful characteristics. Membrane procedures are becoming increasingly popular because to their efficiency in removing germs, pathogens, natural organic matter, and particles. In our thesis we try to use membrane technology to create water filtration which may use in to save industrial water, due to forth industrial revolution saving water is most important issue to save the nature and wildlife. The prime aim of filtration is separation of micro particle from water.

In our studies, heat press lamination was subjected to two distinct pressures and three temperatures. Air permeability, surface pore size, water filtration, and contact-angle tests were used to explore the effects of lamination pressure on the breathability, water permeability, and surface wettability of multi-layered nanofibrous membranes. Moreover, the effects of the laminating pressure on breathability, and water permeability, surface wettability of multi-layered nanofibrous membranes were investigated with air permeability, water filtration, surface porosity, contact-angle experiments. In our work, we used PA6 and PVDF and PAN nanofibers with different surface areas i.e., 1.0 GSM, 1.5 GSM, 2.0 GSM, and 3.0 GSM at 110°C, 125°C, and 135°C temperature. After testing the filtration capacity of all membranes, we get nine best samples out of thirty-six samples, considering the best micro particle separation capacity of all the membranes with high flux.

Key words: Electrospinning, microfiltration, membrane, flux, permeability, microparticles.

Abstrakt

Jak dokazuje rostoucí vědecký a průmyslový výzkum v posledních letech, membrány z nanovláken vytvořené technikou elektrostatického zvlákňování se zavázaly k novým aplikacím pro vývoj technologií. Membrány jsou velmi úspěšné díky svým vlastnostem, které zahrnují malou velikost pórů, velký specifický povrch a vynikající filtraci. Tento nanovláknový filtr je nejvíce fascinující studií v předchozím desetiletí kvůli dostupnosti surovin z nanovláken a zvláštním užitečným vlastnostem. Membránové postupy jsou stále oblíbenější, protože jsou účinné při odstraňování choroboplodných zárodků, patogenů, přírodních organických látek a částic. Tato diplomová práce se snaží použít membránovou technologii k vytvoření vodní filtrace, která může sloužit k úsporám průmyslové vody, protože v důsledku průmyslové revoluce je úspora vody nejdůležitějším problémem pro záchranu přírody. Hlavním cílem filtrace je separace mikročástic z vody.

V této studii byla laminace tepelným lisem vystavena třem odlišným tlakům a teplotám. K prozkoumání účinků laminačního tlaku na prodyšnost, propustnost pro vodu a smáčivost povrchu vícevrstvých nanovláknových membrán byly použity testy propustnosti vzduchu, filtrace vody, velikost povrchových pórů a kontaktní úhel. Kromě toho byly zkoumány účinky laminačního tlaku na prodyšnost, propustnost pro vodu a smáčivost povrchu vícevrstvých nanovláknových membrán pomocí experimentů s propustností vzduchu, vodní filtrací, pórovitostí povrchu a kontaktním úhlem. V této práci jsou použita nanovláknová PA6, PVDF a PAN s různými povrchovými plochami, tj. 1,0 GSM, 1,5 GSM, 2,0 GSM a 3,0 GSM při teplotě 110°C, 125°C a 135°C. Po testování filtrační kapacity všech membrán bylo získáno devět nejlepších vzorků ze třiceti šesti vzorků, přičemž se bere v úvahu nejlepší schopnost separace mikročástic všech membrán s vysokou propustností.

Klíčová slova: elektrospining, mikrofiltrace, membrána, tok, propustnost, mikročástice.

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LISTS OF SYMBOLS

Symbols	Long Name	Units
PA6	Polyamide 6	
PVDF	Polyvinylidene fluoride	
PAN	Polyacrylonitrile	
MF	Microfiltration	
NF	Nanofiltration	
Nm	Nanometer	nm
μm	Micrometer	μm
GSM	Gram per square meter	g/m^2
Flux	membrane flux	$\text{Lm}^{-2}\text{h}^{-1}$
K	membrane water permeability	$\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$
H	hour	h
Sec	second	s

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1. INTRODUCTION

Nanofiber membranes by electrospinning engineering are being devoted to new application for emerging technologies, as demonstrated by rising scientific and corporate research in recent years. Membranes are so effective due to their properties effectively characterized for instance, narrow pore size and specific surface area and good filtration properties as well. Due to availability of raw materials of nanofibers and special convenient properties, nanofibrous filter is the most interesting study in last decade. Membrane processes are popular in these days because effectiveness of removal bacteria, microorganisms, organic material, particulates, and which can impart on the color, and odors to water, tastes, and react with the disinfectants to form the disinfection byproducts [1].

Microfilter has been developing at industrial commercial scale for several purposes. Removing of bacteria from milk and selective separation of casein micelles from soluble proteins are the clear example of using micro-filters [2]. Although most water is filtered for human consumption, it may also be used for a number of other purposes, such as satisfying the needs of medicinal, pharmaceutical, chemical, and industrial uses [3].

Surface of nanofibers is extremely high. Its aspect ratio is much more than conventional fibers. The reason behind the not using in water is due to their mechanical weakness which cannot stand under water. Two different pressures and three different temperatures were applied to heat press lamination in our experiments. The thermal lamination process is one of the most efficient, repeatable, timesaving, environmentally safe and cost-effective methods of surface adhesion. The adhesive polymer or polymer web is typically applied between three surfaces in this system. Using heat and pressure, the surfaces adhere together. In our thesis we use polyethylene terephthalate (PET) and adhesive web (copolymer) and nanofiber. Due to low melting point of adhesive web, it become melt and nanofiber and PET are bonded together [4]. It was found that both the supporting material and density of the nanofiber network had an effect on the water permeability of the multilayer nanofibrous membranes. The lower area weight of an open structure supporting components has a greater water flow and permeability. Kanafchian et al. [5] used a heat-press method for lamination polyacrylonitrile (PAN) nanofiber to the polypropylene spunbond at different laminating temperatures. It has been found that although applied

temperature is smaller than the melting point of the polypropylene spunbond, the nanofiber web remains unchanged. There is a wide volume of research related to enhancing the strength of nanofibers; however, the number of publications is still small relative to those related to lamination technology.

2. THEORITOCAL PART

2.1 Nonwoven

Nonwovens are sheet, web or bat of natural and/or man-made fiber if filaments, excluding paper, that have not converted to yarn and they are bonded with each other by many several means. For example, adding adhesive or thermally fusing, stitching etc. Nonwoven are flat, specific porous sheets that are produced from separate fibers or from molten polymer or plastic film [6].

Nonwovens are progressing rapidly to support filter media producers in providing increased efficiency. This technology is also use for thin sheet as a membrane which is use for air filtration and hygiene product like mask, wound dressing, and some medical sectors layer sometimes nonwovens are use as filter and support of membrane. Nonwovens provide many unique technical qualities in comparison with fabric filters, including increased permeability, a more specific surface area and controllable pores and smaller pore sizes, and the advantages of a higher filtration efficiency, lower power consumption and better cake release properties on were, in comparison with woven textile filters. Nonwovens and membranes both have their own benefits, which are combined to enable membranes to work at their best in a given application. Nonwoven fabrics are typically used as a secondary support to provide mechanical strength to comparatively poor membranes [7]. The most important aspect of nonwoven cloth is manufactured directly from fibers in a continuous production line. When producing nonwovens, certain traditional textile activities, such as carding, painting, roving, spinning, weaving, or knitting, are partly or entirely removed. For this cause, the option of fiber is very critical for non-woven manufacturers. The widely used fabrics contain natural fibers (cotton, jute, flax, wool), synthetic fibers (PES), polypropylene (PP), polyamide, radius, unique fibers like as glass, carbon, nanofiber, bi-component, superabsorbent fibers. Cheaper raw materials have not only brought major changes to the product, but have also enriched the demand that we need[8].

2.2 Spun bond

Spun bonding method is used for man-made filament fibers which melt under heat, such as polyester. Spun bond fabrics are produced by depositing extruded, spun filaments onto a collection of belts in a uniform random manner followed by bonding the fibers. Spun-bond fabrics are characterized by tensile, tear, burst strengths, elongation-to-break, thickness, porosity and the stability to heat and chemicals. Spun bond products are used in carpet backing, geotextiles, and disposable medical/hygiene products also. Since the fabric production is combined with fiber production, the process is generally more economical than when using staple fiber to make nonwoven fabrics [9]. In our experiment we used spun bond Polyethylene terephthalate(spunbond) as a layer of our membrane.

2.3. Adhesive web (copolyester)

Adhesive(copolyester) web is a thin layer sheet of polymer dispersion adhesive is a white colored mixture that is based on polyester. Widely recognized as one of the most efficient ways of bonding purpose like as woods, sheet [10]. These are high-performance hot-melt adhesives. Polyesters are usually divided into amorphous, weakly crystalline and highly crystalline grades. The advantages of use are in particular a good price-performance[11]. These adhesive webs we used for making thermal bonding between the supportive layer nonwoven and nanofiber

2.4 Electrospinning

2.4.1. Needle Electrospinning

The fundamental theory of fiber forming in this phase is the "electrostatic force" of charges. As high voltage is applied to the device, the pump forces the solution out of the needle due to the surface tension of the solution. When the solvent comes at the tip of the needle, the opposite loaded collector is positioned. The aim of which is to collect the expelled fibers. As the solution is supplied with high voltage, the solution emerges from resolving the surface tension and forms a cone like a structure called "Taylor Cone" (drop like structure at the tip of the needle) as shown in Figure 1 [12].

Electrospinning technique is a novel method in which electrostatic forces are used to manufacture extremely fine fibers from polymeric solution or melt solution and the fibers have developed a thinner nanometer diameter and a high surface-to-volume ratio. The critical parameter for generating electrospinning is DC electrospinning voltage and is within a range of several tens of kilovolts. This technology is very similar to electrostatic precipitates and pesticide sprayers, the basic idea is that high electrostatic repulsive forces overpower the weaker surface tension of the charged polymer solution. The solution used for the electrospinning phase must bear an electrical charge and have adequate viscosity so that it can be extended without splitting into small drops at the tip of the needle [11]. There are currently two primary electrospinning configurations vertical and horizontal. The setup of the electrospinning device consists of three key components as follows.

1. High voltage power supply
2. A spinner ate
3. Grounded collector plate.

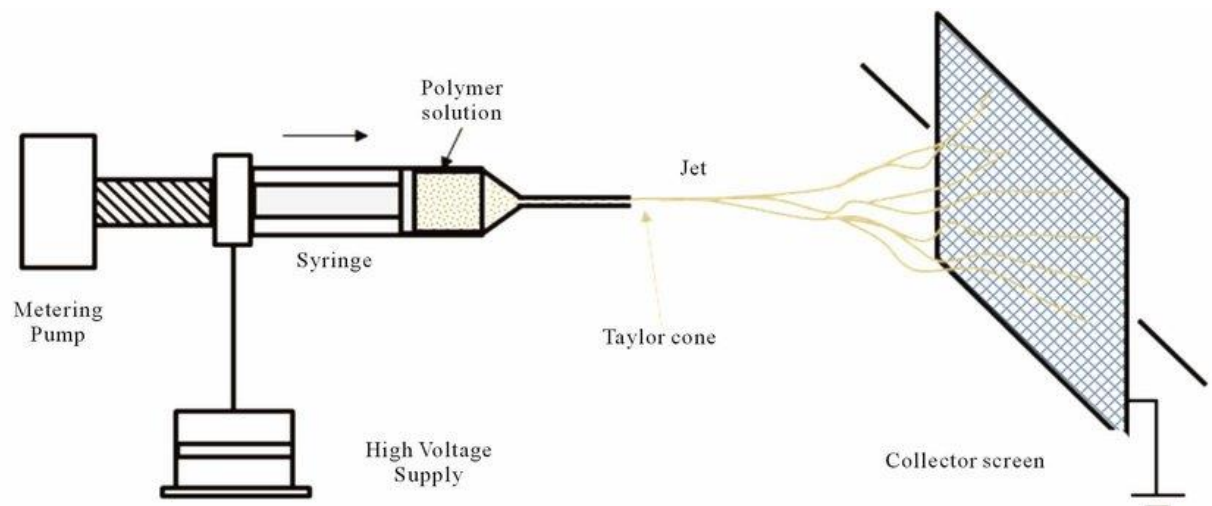
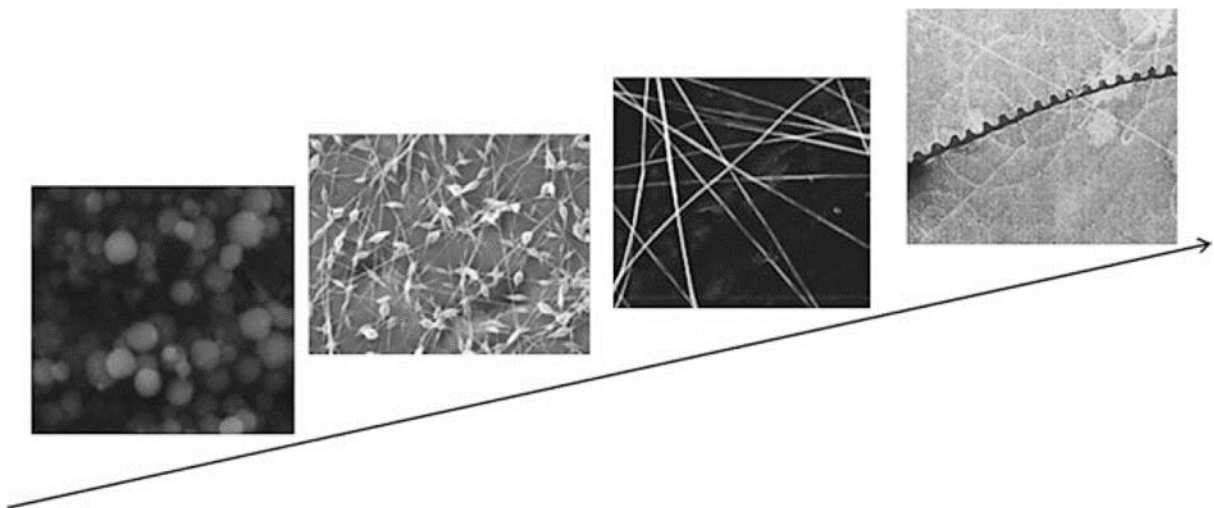


Figure 1: Basic principles of Electrospinning [13].

2.4.2. Material parameters of Electrospinning

2.4.2.1 Concentration of Solution

The size and shape of the produced fibers are directly proportional to the solution concentration. It is primarily focused on three parts: when the concentration is extremely low, when the concentration is extremely high, the viscosity is low and the surface tension is high, electrospray occurs. Smooth nanofibers are generated when the solution concentration is appropriate, but helical curved ribbon-like structures are found when the concentration is too high [14]. The flow rate of the solution through the spinnerets is also affected by the concentration of the solution; if the concentration is less than, the solution breaks into small droplets before reaching the collector, and this small breaking generates the beads. When we raise the concentration of the solution, beadles fibers form due to correct flow of the solution, but when we exceed this limit, the flow rate of the solution is affected, the solution is dried at the tip of the needle, and the flow is blocked. Scientists discovered that the link between fiber diameter and concentration is a power law relationship, with diameter of the fiber increasing as concentration increases in gelatin electrospinning. The solution's viscosity and surface tension also determine the concentration range, which aids in obtaining a continuous fiber range. In Figure 2, the arrow indicates the



increasing concentrations [15].

Figure 2: SEM images of fibers with increasing concentration [15].

2.4.2.2 Molecular weight

The molecular weight of any solution for electrospinning is not always important for the spinning of the fibers if the intermolecular forces of interaction given by the oligomers is sufficient. The solution viscosity is affected by the molecular weight of the polymer; if the solution concentration remains constant and the molecular weight of the polymers is reduced, beads form; when the molecular weight is increased, proper fibers form; and when the molecular weight is increased again, a ribbon-like structure form. In the Figure 3-a the molecular weight is relatively high and beads form, on the other hand the Figure 3-d has optimum molecular weight and viscosity which result is proper nanofiber [16].

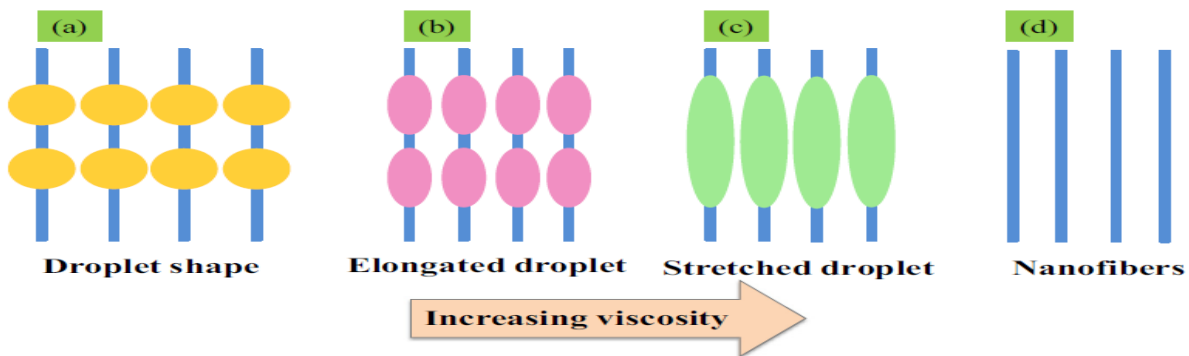


Figure 3: Change the shape of droplet with viscosity [15].

2.4.2.3 Surface tension

The force imposed on the plane of the surface per unit length is defined as the surface tension of the solution. The applied voltage in the electrospinning process should be high enough to overcome surface tension and allow the spinning solution to create nanofibers. Varied solutions have different surface tension values, and by keeping the solution concentration constant and lowering the surface tension, beaded fibers can be transformed into smooth fibers. Surface tension is a feature of the solution's solvent that affects the electrospinning process by lowering the surface tension of the solution, we can create fibers without beads. In general, the high surface tension of the solution impedes the electrospinning process due to jet instabilities and

droplet spreading. The solution's surface tension governs the development of beads, droplets, and threads [16].

2.5. Process parameter of Electrospinning

2.5.1 Voltage

The applied voltage is a crucial parameter in the electrospinning process. Jet ejection through the Taylor cone is only feasible when the applied voltage exceeds the threshold voltage. There are various inconsistencies about the effect of applied voltage on fiber diameter. According to some scientists, the applied voltage has no effect on fiber diameter in polyethylene oxide electrospinning. In the case of polyvinyl alcohol, scientists claimed that high voltage causes large diameter fibers to form. However, another group discovered that high voltage causes an increase in electrostatic repulsive force, resulting in narrow diameter fibers to form, while others claimed that bead formation occurs at high voltage [15], [17]. When we increase the voltage above the critical value, bead formation occurs, as does the diameter of the fiber, resulting in a reduction in the size of the Taylor cone at the end of the needle and an increase in jet velocity for the same flow rate [5]. In the Figure 4-f the optimum voltage is applied, if the voltage is not optimum the Taylor cone will create bead. Many research publications showed that the higher the applied voltage, the more stretching in the solution and the formation of thin fibers. If a low viscosity solution is utilized with a higher applied voltage, secondary jets and thin fiber diameter are formed; at a high voltage rate, the stretching of the solution droplets increases, which may result in greater acceleration towards the collector reason is high potential difference [15], [16] [17].

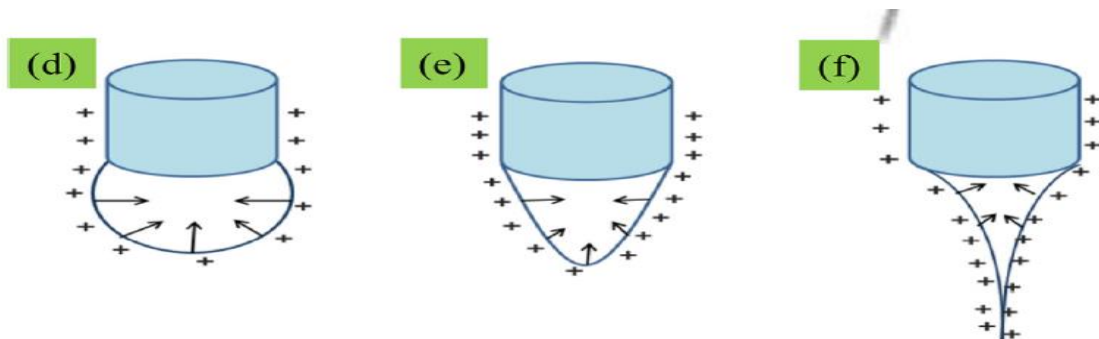


Figure 4 : Effect of size on the droplet [17].

2.5.2. Solution flow rate

Another critical parameter is the solution flow rate, which influences the velocity of the jet and the material transfer rate. A lower flow rate is beneficial for the electrospinning process because it allows for more time for the solvent to evaporate. In the study of polyester, the diameter of the fiber grows with decreasing flow rate, and the morphological structure also changes slightly by changing the flow rate of the solution, and high flow rate gives the bead due to insufficient drying time. To generate uniform and beadless fibers, we must employ a critical flow rate for the polymer solution, which changes according to the polymer solution. A. Haider and S. Haider[15] mentioned that if the flow rate increases, a ribbon-like structure and unspun droplets appear. This is due to reduced stretching of the solution and no evaporation of the solvent in the time between the needle and the collector.

2.5.3 Tip to collector distance

The distance between the tip and the collector influences the route of the jet and the time necessary to travel before resting on the collection. At constant voltage, electric field intensity is inversely proportional to electric field strength. If the voltage remains constant while the distance changes, the properties of the fiber are quite similar to those of altering the voltage while maintaining a constant distance. As the distance grows, the fiber diameter decreases first, then increases due to a lowering of the electric field strength [17]. If the distance between the tip and the collector is too short, the fiber will not have enough time to dry before reaching the collector, and if the distance is too long, bead formation will occur; hence, the ideal distance is essential to ensure smooth fiber formation, in the Figure 5, the standard distance from tip to collector must be an optimum value, the distance and tip collector should be proportional [16].

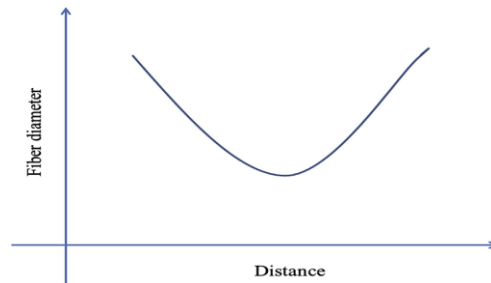


Figure 5: Graphical representation of relation between diameter and distance [16]

3.0 Membranes

Membrane separates into two phases and stop penetrate several types of chemicals, solutes, proteins, viruses, and bacteria. In order to classification of membrane are homogenous, heterogeneous and symmetric or asymmetric in physical structure [18].

The efficiency of membrane is depending on membrane itself as well as conventional methods. The procedure of separation is very straight forward. Membrane performs double duty for separation. One is a semi permeable layer between two layers and the other is transportation between two phases. Membrane absorbs liquid and allows to pass liquid and catch the particles. The procedure is normally carried out under atmospheric conditions. Membrane separation methods are an effective, and beneficial approach for oil-water separation. Membrane manufacturing is one of the most advanced technology used in the food processing, chemical and fuel cell industries for the isolation of oil-water, waste water or emulsion [19].

3.1. Membrane Technology

A membrane is a layer that divides two phases and selectively restricts the transport of certain chemicals. Membranes may be homogeneous, heterogeneous, symmetric or asymmetric in form, solid or liquid, and have a positive or negative charge, as well as be neutral or bipolar[18].

The effectiveness of membrane separation is largely based on the membrane itself, and it is more effective than traditional approaches.

The separation procedure is simple. The membrane has a dual purpose in terms of isolation. The first is to act as a semi-permeable barrier for two phases, and the second is to transport two phases. The filter essentially traps dissolved solids or other particles in the emulsion and allows water to pass through the membrane [19].

In most cases, the procedure is carried out under normal ambient conditions. Membrane separation processes are an effective, reliable, and beneficial approach for oil-water separation. Membrane technology is one of the most efficient technologies for separating oil-water emulsions, which are widely used in the dairy, medicinal, desalination, and fuel cell industries.

Membrane separation has a higher performance, consistent effluent content, and lower energy consumption as compared to chemical and other therapies. Membrane technology is the most effective way to isolate particles wastewater for the reasons mentioned above [21].

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are pressure-driven membrane processes. Generally, the processes are almost similar. The main difference between them is membranes pore size as shown in the Figure 6 [19], [22].

The thickness of the membrane can vary as small as 10 microns to a few hundred micrometers, and pore size is over than 50 nm [13], [21].

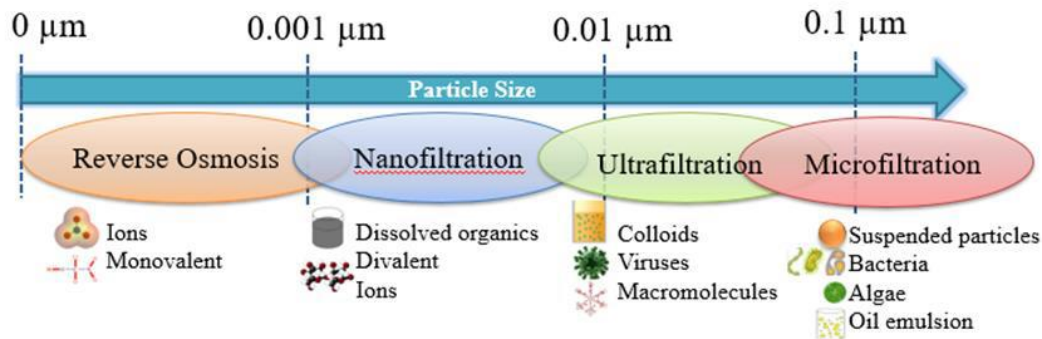


Figure 6: Filtration type depending on pore size [22].

In microfiltration (MF) and ultrafiltration (UF), the basic mechanism is the sieving mechanism which is the rejection of molecules whose size is greater than pores[23]. Sieving mechanism is very easy to easy way to permeate the liquid. If diameter of particle is higher than the filter that will catch by surface of filter [24]. Figure 7 indicates the process of membrane separation.

In electrostatic process, membrane will charge when they are touch into the water. Polymer membranes that which are negatively charged are usually above pH 4-6, and those that are positively charged below are than pH. The membrane charge influences membrane performance when low cut-off membranes are used at low salt concentrations. The flux is also affected by the charge on the membrane. When electrostatic repulsive forces are present, both flux and retention are expected to improve. When electrostatic repulsion is greater at pH 7 than at pH 5,5, fouling is somewhat less. When cationic and anionic additives are used, a highly charged membrane may

be fouled rather than a less charged membrane. Cationic polymeric retention aids can bind to the negatively charged membrane's surface and induce fouling. Salt, pH, macromolecules, and small particles in the 1 nm to 1 μm range influence the rate of precipitation and fouling. The equilibrium of the water can be increased by softening it and changing the pH [25], [26]. Because of coagulation and flocculation process, colloids are removed from waters. It has an effects on colloidal stability. Sometimes it can improves the efficiency of the filtration process [27]. This mechanism in figure which we attached below.

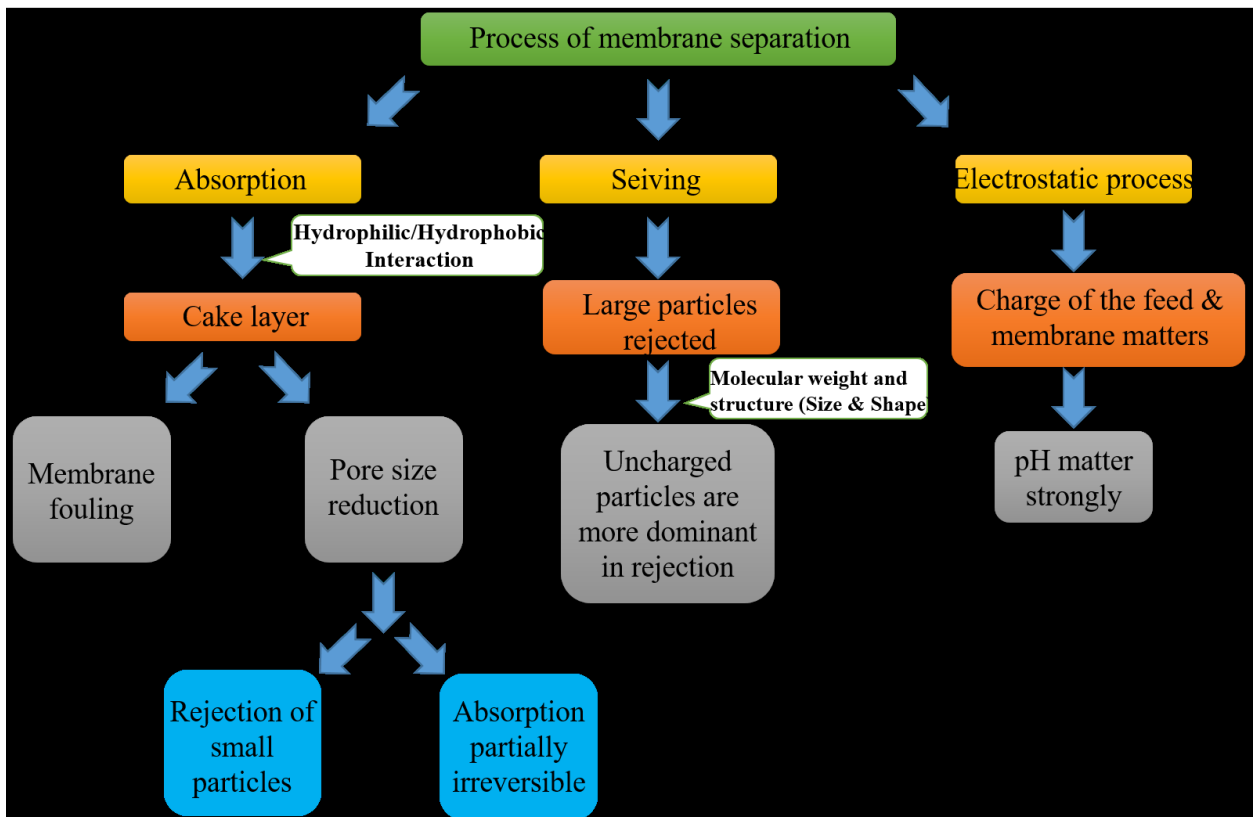


Figure 7: membrane separation process [19].

The membrane is a thin interface that moderates chemical species' permeation as they come into contact with it. The interface can be chemically or mechanically heterogeneous, or it can be entirely uniform in composition and structure, or we can call it molecularly homogeneous. It can, for example, contain holes or pores with observable dimensions or be made up of a layered structure [28]. Membrane is classified in several section, here we are going to discuss below (in Figure 8)

3.1.1 Types of membrane

3.1.1.1 Isotropic membrane

- Microporous membrane
- non-porous membranes
- Electrically Charged membrane:

3.1.1.2 Microporous membrane

In terms of structure and function, the microporous membrane is very similar to the traditional filter. The pore distribution is random, strongly voided, entangled and has a rigid structure. The explanation for the discrepancy between the pores and the traditional filter is exceedingly small and the diameter is 0.01–10 μm . The rejected particles of the membrane are all particles greater than the largest pores. Partially rejected particles are smaller than the larger pores, but larger than the smaller pores. The particles that move across the membrane are much smaller than the smallest pores. Therefore, the isolation of solutes by microporous membranes relies primarily on the distribution of molecular size and pore size. Generally, by microporous membranes, only molecules which vary considerably in size can be effectively separated by ultrafiltration and microfiltration [20].

S. Ripper and G. Schultz were used polyester as a microporous membrane in biotechnical industry in filtration and porosity of these membranes is much lower than that of polymeric membranes, but its thermal stability allows them to be used also at the high temperatures [29].

Microfiltration Membrane is known as pressure-driven separation process, which is widely applied in concentrating, purifying, or separating macromolecules which are suspended particles in the solution. MF must be operated by membrane. MF membranes typically have micro pore sizes 0.1 μm lower to 10 μm . MF processing is popular by using in food industry for applications such as wine, juice and for waste-water treatment , and the separation of plasma from blood for therapeutic and commercial uses too. Dissolved pollutants are not removed by MF. A variety of water treatment applications include microfiltration water treatment for drinking water is a typical example of microfiltration [20].

3.1.1.3. Dense, non-porous membranes

This type of membrane consists of a thick film in which the permeants are transferred through diffusion under the driving force of a strain, concentration, or electrical potential gradient. The isolation of the different components of the mixture is directly related to their relative transport rates within the membrane, which are determined by their diffusivity and solubility in the membrane substance. Thus, this type of membrane can isolate similar size permeants if their concentrations in the membrane material (i.e. their solubility) are substantially different. Dense membranes have the downside of low flux unless they can be rendered incredibly thin. For this function, dense membrane properties are integrated into the upper "skin" layers of asymmetric membranes [30].

3.1.1.4. Electrically Charged membrane

This type of membrane is often referred to as an ion-exchange membrane. They can be thick or microporous, but primarily are very finely microporous, with pore walls holding which positive or negatively charged ions. A membrane fixed with positively charged ions is name an anion-exchange membrane because it binds anions (negatively charged ions) to the surrounding fluid. The opposite is true of the cation-exchange membrane. Separation is primarily accomplished by excluding ions with the same charge as fixed ions on the membrane structure which is caused by the charge and concentration of ions in the solution. This form of membrane is used for electrolyte solutions in electrodialysis [30].

3.1.1.5. Anisotropic Membrane

A traditional anisotropic membrane has a very densely finely structured surface support on an open porous structure that is much thicker. The rate of transport of the organisms across the membrane depends on the thickness and is inversely proportional to the thickness of the membrane. In membrane separation processes, high transport rates are needed for economic reasons. The membrane should then be as small as possible. The production of mechanically solid, defect-free films in traditional film production technology is restricted to approximately 20 μm thickness.

Creation of new membrane processing methods to produce anisotropic membrane structures. Anisotropic membranes are composed of an incredibly thin surface layer and a much thicker, porous support. The surface layer and its substructure can be formed in a single process or separately. One of the special quality of this membrane is high flux and it's possible to use in commercial purpose [31].

3.1.1.6. Ceramic, Metal, and liquid Membranes

This membrane is become popular in last few years. Ceramic and special microporous membrane are typically used for microfiltration and ultra-filtration where they are solution resist and stabilize in thermally. Gas mixer and dene metal are typically example of separation of metal membrane. In addition, transport porous and supported liquid are developed [20], [31].

Seung-Jin and Mehmet Dilvar [32] used ceramic membrane and polymeric membrane in filtration experiments, there they got The fouling created by ceramic membrane which was initially characterized by a pore blocking mechanism, that was converted to a cake filtration mechanism later in the filtration process.

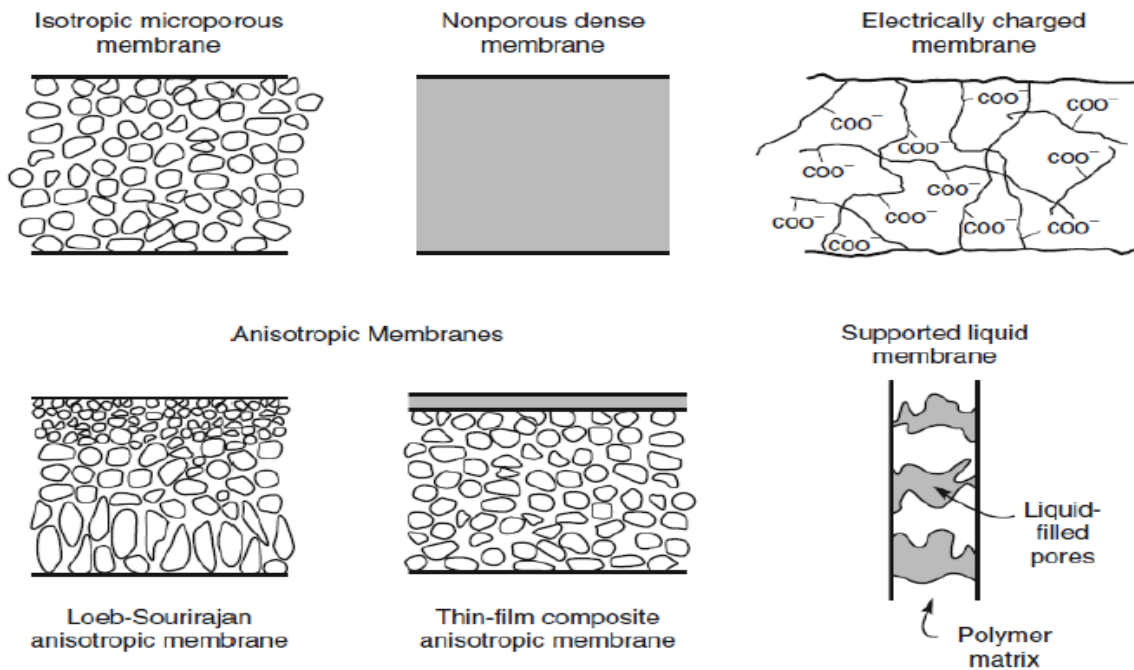


Figure 8: Types of membranes [20].

Under the conditions tested in this analysis, cake resistance was the most prevalent type of total resistance for ceramic membranes, though it is possible to remove by physical cleaning it's not a durable process for filtration.

4. Filtration process/method

Two different approaches are categorized into the membrane filtration process: dead-end and crossflow filtration. In dead-end filtration (in Figure 9 right side), feed solutions are applied perpendicular to the membrane surface, while in cross-flow filtration feed solutions are applied horizontally (in Figure 9 left side) to the membrane surface. In the dead-end filtration process, membranes appear to exhibit the fouling effect in particular because of aggregation on the membrane surface. The fouling impact eventually wraps up with a filtration pause. The crossflow filtration system has decreased fouling as much as possible and improved efficiency despite the dead end [33]

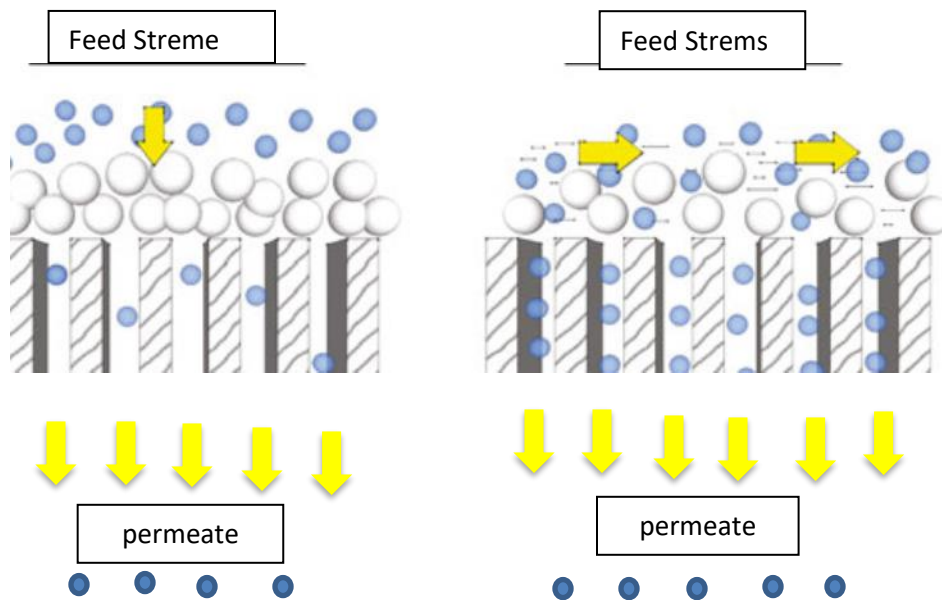


Figure 9: Different filtration methods [33].

Many gas isolation, pervaporation, and reverse osmosis processes use thick membrane to isolate.

5. Nanofibers in Membrane Technology

Due to its ability to fabricate nanostructures with special properties such as a high surface area and porosity, electrospinning has been developed as one of the most effective techniques for the fabrication of polymeric nanofibers. Nanofiber fabrication and implementation was influenced by the method and operational parameters in a variety of areas, including sensors, tissue engineering, wound dressing, protective clothing, filtration, desalination, and distillation [22].

Polymeric fiber for example polyester, polyvinylidene fluoride etc. synthetic polymeric fiber can be used to prepare microfilter membrane, but the most important is membrane need have capacity to absorb the liquid unlike hydrophobic or oilphobic. But main disadvantage of nanofiber membrane is not so durable and it's a challenge to make recycle for long time [34]. Table 1 shows the prepared nanofiber membranes and their filtration process.

Table 1: Types of nanofibers and filtration process.

Type of nanofiber	Type of filtration/foulant	Reference(s)
PVDF, PAN, PA6 and PUR.	Preparation of Nanofibrous Membranes for Oil/ Water Separation	[20]
polyvinylidene fluoride (PVDF) polymethyl methacrylate (PMMA) polysulfone (PSf) polyacrylonitrile (PAN)	Functionalized electrospun nanofiber membranes for water treatment	[35]
Polyurethanes, Polyethersulfone, Polyacrylonitrile	Electrospun polymeric nanofibrous membranes for water treatment	[12]
polytetrafluorethylene (PTFE), polyvinylidene fluoride (PVDF)	A review on electrospinning for membrane fabrication	[36]

polyvinylidene fluoride (PVDF), polyvinylidene fluoride (PVDF)	Refining sugarcane juice by an integrated membrane process: Filtration behavior of polymeric membrane at high temperature	[37]
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5.1. Nanofibers as Microfilter

Nanofibers are fibers with small diameters in the nanometer range. Nanofibers can be generated from several polymers and hence have different physical and thermal properties and application potentials. It is possible to produce polymer from polyamide, polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and chitason and collagen etc. [38].

At the beginning of the last decade electrospinning nanofiber has become more famous in microfiltration. PVDF is one of the earliest experiments as a microfilter. This membrane was successful almost 90% success on filtration purpose.

Nanofiber membrane (NFM) high pore size and simple production method. Due to mechanical property NFM is not so sustainable but it has good application. In addition, flux performance is also great in NFM. The porosity of membrane and fiber diameter have a tremendous impact on the pore size, while thickness is almost constant [35].

The mechanical weakness of nanofibers restricts their application in water domain area. For this reason, it is necessary to improve their mechanical strength. Next sub-title we prepared the various method to improve nanofiber strength with their advantages and disadvantages.

5.2. Improving strength of Nanofiber membrane

There are several techniques to strength nanofiber membrane. For instance, blend polymer is one of the most popular for its low price but there are very small amount polymer is available to do the procedure[39], [40]. One another method is by using epoxy composite. In this method electrospinning need to laid down on epoxy agent and it is necessary to keep that condition around 16 hours [13]. Charles et al. [41] used a dip coating technique to increase the mechanical efficiency of nanofibers. They described the mechanical properties of a composite system

consisting of hydroxyapatite (HA)-coated poly (L-lactic acid) (PLLA) fibers in a poly(-caprolactone) (PCL) matrix. A biomimetic process was used to coat the HA fibers and a dip-coating technique was used to apply PCL to the coated fibers. The composite was shaped into a bar using low temperature compression molding. The downside to this strategy is that it is a time-and a time-and chemical-consuming method [42]. Thermal lamination is most popular effective system as it is saving energy with high production capacity and low cost as well. Here, two layers are used to laminate with each other by using an adhesive web (layer of co. polymer around 12 GSM) [42]. A bi-component spunbond polyethylene (PE)/polypropylene (PP) was used by Jiricek and Yalcinkaya et al. [42] as a supporting layer for nanofiber layers. For the lamination process, a fusing system was used. Due to the low melting point of PE, it binds to the outer surface of the bi-component. Micro and nanofilters were used with the resulting multilayer nanofibrous membranes. The supportive material and the stiffness of the nanofibers impact the permeability of the multilayer materials to water and air [4], [43]. Yoon et al. laminated by an adhesive web, nanofibers with different polyurethane (PUR) fiber densities on various textile surfaces. The findings revealed that the different configurations of the multilayer nanofibrous membrane structure had a major effect on the textile surfaces' degrees of breathability and waterproof effect [44].

5.3. Nanofiber industrial for water treatment.

There were plenty of research was held by scientist in before to develop nanofiber membrane. Among of them Liquidity Filter is developed by Massachusetts Institute of Technology (MIT), for bacterial filtration around 0.2 micrometer, they worked with PAN. Though PAN was capable to remove protozoan cyst containing dies, which is useful for developing countries. Water purify Technologies Inc. also provides nanofiber filtration products, including a stock of nanofiber filtration systems co-developed by NASA. Though the association with a space agency may be deemed as a marketing tool, it demonstrated the applications of water filtration Electrospinning nanofiber membrane (ENMs) technology is out of this world. These are examples of current market technologies using ENMs systems.

Nanopareil, formerly known as nanofiber separations, manufactures random electrospun nanofiber membrane mats that sell the scale and adsorption properties of these materials and supply them to the water purification and desalination industries. Toyobo, a Japan-based firm,

also has its own proprietary HOLLOSEP nanofiber filtration membrane that operates under the principles of reverse osmosis. The electrospun fibers consist mostly of cellulose triacetate, are able to withstand high chlorine concentrations in water to avoid biofouling and have been used effectively on a wide scale both in Japan and in the global desalination industry.

One more example is the start-up technology creation company GABAE Industries, which is also exploring nanofiber technology for filtration purposes through electrospinning in order to remain on the top-of-the-line technology market for its customers and the ever-important filtration industry-not only for water, but also for air filtration. Water recycling from the air using nanofibers is also feasible, as it has been demonstrated that a system made from ENMs will condense the moisture in the air into drinking water[45].

5.4. Filtration Process of Nanofiber Membranes

High permeability is related to resistance. Permeability is defined as the term permeability coefficient, which is directly proportional to fluid flow rate, filter medium, fluid viscosity and thickness and vice versa to fluid density[46].

Filtration permeability influence by several means

- 1.Filter size
- 2.filter temperature
- 3.filtration time

5.4.1. Filtration permeability

In industrial operations, cake filtering is widely used to remove particulate materials from fluids. The formation of a filter cake is frequently followed by a reduction in the filter's overall permeability, resulting in an increased pressure drop across the filter medium. A linear pressure drop profile is expected over time for an incompressible filter cake that builds up on a homogenous filter fabric (surface filtration mode). However, curved pressure drop profiles have been observed in several trials. Cake compression and/or depth filtering are commonly attributed to pressure decrease profiles with increasing slope. Pressure drop profiles with decreasing slopes

may only be attributed to filter inhomogeneities. Filter cake patches and/or an inhomogeneous filter cloth can cause such inhomogeneities [50].

6. Aim of thesis

Save water save life is the demand of forth industrial revolution. But this process is neither easy nor cheap. Due to this reason, the third our country namely Bangladesh are destroying water sources and environment. But if we can do proper use of membrane technology in industrial purpose for water filtration then environment will exempt from this curse. In developed countries the membrane technologies are used and vast for water filtration.

The market of demand is high due to high efficiency and high permeability, high particle rejection and mechanical strength as well. Talking account all of these qualities we choose this thesis filtration by nanofiber membrane.

There are several advantages of using membrane

- A) As membrane has good adsorption capacity so, membrane of nanofiber plays an important rule to pass water or liquid.
- B) High porous as well as narrow pore size of nanofibers allow good permeability.
- C) according to previous studies easy to modify the surface.
- D) variety polymeric solution can use to prepare of nanofiber to get precious results.
- E) After all, higher filtration efficiency is most important to work with nanofiber filter.

Based on the above quality, we have selected various nanofiber. The selection of nanofiber was based on previous studies, availability, low cost, specific fiber densities (g/m²-gsm). PA-6, PVDF and PAN are the prime study material of our thesis.

To sum up, our objective was developed the mechanical strength and get best membrane for water permeability and know about optimum temperature for lamination process and select highly efficient membrane for rejection micro particles. Herein, we tried to determine effect of lamination conditions and each component of hybrid layers on the membrane performance.

7. Materials and Methods

Nanofibers at various g/m^2 (GSM) have been taken from Institute for Nanomaterials, Advanced Technology and Innovation, TUL. Nanofibers were laminated using an adhesive web and supporting layer at various condition to form hybrid membrane structure. Table2, 3, and 4 indicates the each polymeric nanofiber and their GSM, type of adhesive, type of supporting layer and, abbreviation of membranes and we use 30 KN pressure for 2 minutes and 50 KN for 1 minutes for each and every sample. The reason is to slowly fixing the lamination process without damaging the nanofiber layer.

Table 2. Nanofiber membranes and their abbreviations for Polyamide 6

Type(s) of polymeric nanofiber	GSM	Temperature($^{\circ}\text{C}$) used to prepare samples	Type of adhesive web	Type of supporting layer	Preparation condition of Samples (lamination Condition)	Abbreviation of sample(s)
Polyamide 6	1.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110°C temperature.	PA6-1A-110
Polyamide 6	1.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125°C temperature.	PA6-1A-125
Polyamide 6	1.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135°C temperature.	PA6-1A-135
Polyamide 6	1.5	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110°C temperature.	PA6-1.5A-110
Polyamide 6	1.5	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125°C temperature.	PA6-1.5A-125
Polyamide 6	1.5	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135°C temperature.	PA6-1.5A-135
Polyamide 6	2.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110°C temperature.	PA6-2A-110
Polyamide 6	2.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125°C temperature.	PA6-2A-125
Polyamide 6	2.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135°C temperature.	PA6-2A-135
Polyamide 6	3.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110°C temperature.	PA6-3A-110
Polyamide 6	3.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125°C temperature.	PA6-3A-125

Table 3. Nanofiber membranes and their abbreviations for PVDF

Type(s) of polymeric nanofiber	GSM	Temperature ⁰ C used to prepare samples	Type of adhesive web	Type of supporting layer	Preparation condition of Samples (lamination Condition)	Abbreviation of sample(s)
Polyvinylidene fluoride (PVDF)	1.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PVDF-1A-110
Polyvinylidene fluoride (PVDF)	1.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PVDF-1A-125
Polyvinylidene fluoride (PVDF)	1.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PVDF-1A-135
Polyvinylidene fluoride (PVDF)	1.5	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PVDF-1.5A-110
Polyvinylidene fluoride (PVDF)	1.5	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PVDF-1.5A-125
Polyvinylidene fluoride (PVDF)	1.5	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PVDF-1.5A-135
Polyvinylidene fluoride (PVDF)	2.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PVDF-2A-110
Polyvinylidene fluoride (PVDF)	2.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PVDF-2A-125
Polyvinylidene fluoride (PVDF)	2.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PVDF-2A-135
Polyvinylidene fluoride (PVDF)	3.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PVDF-3A-110
Polyvinylidene fluoride (PVDF)	3.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PVDF-3A-125
Polyvinylidene fluoride (PVDF)	3.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PVDF-3A-135

Table 4. Nanofiber membranes and their abbreviations for PAN

Type(s) of polymeric nanofiber	GSM	Temperature(°C) used to prepare samples	Type of adhesive web	Type of supporting layer	Preparation condition of Samples (lamination Condition)	Abbreviation of sample(s)
Polyacrylonitrile (PAN)	1.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PAN-1A-110
Polyacrylonitrile (PAN)	1.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PAN-1A-125
Polyacrylonitrile (PAN)	1.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PAN-1A-135
Polyacrylonitrile (PAN)	1.5	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PAN-1.5A-110
Polyacrylonitrile (PAN)	1.5	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PAN-1.5A-125
Polyacrylonitrile (PAN)	1.5	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PAN-1.5A-135
Polyacrylonitrile (PAN)	2.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PAN-2A-110
Polyacrylonitrile (PAN)	2.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PAN-2A-125
Polyacrylonitrile (PAN)	2.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PAN-2A-135
Polyacrylonitrile (PAN)	3.0	110	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 110 ⁰ C temperature.	PAN-3A-110
Polyacrylonitrile (PAN)	3.0	125	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 125 ⁰ C temperature.	PAN-3A-125
Polyacrylonitrile (PAN)	3.0	135	Copolyamide	120gsm PET	2 minutes 30 KN pressure and 1 minute 50 KN pressure with 135 ⁰ C temperature.	PAN-3A-135

Nylon 6 or Polyamide 6: Polyamide 6 or Nylon 6, is a semi-crystalline polyamide which has a chemical formula $(C_6H_{11}NO)_n$. Polyamide-6 fiber has higher elasticity, luster properties, and tensile strength.

They are highly resistant to abrasion and chemicals. Fibers can absorb up to 2.4% of water. But that decreases the tensile strength. The glass transition temperature (T_g) of polyamide 6 is 47 °C. The melting point T_m of polyamide 6 is around 215 to 255 °C [47]. The structural formula of polyamide 6 (PA6) is shown in Figure 10.

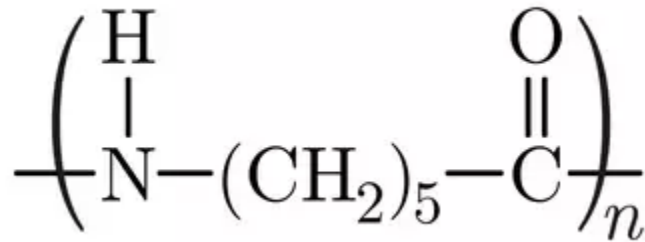


Figure 10. Chemical structure of Polyamide6 [47].

Polyvinylidene fluoride (PVDF): PVDF is special polymer which is used in applications which requires higher purity, resistance to solvents, and hydrocarbons. It is compatible with U.S. Food and Drug Administration and non-toxic. Therefore, for food production it can be used in repeated contact. The glass transition temperature of PVDF is about -35 °C and it is often 50-60% crystalline. The melting point of PVDF is around 177-190 °C. It is not soluble in water. The chemical structural formula of PVDF is shown in the Figure 11 [48].

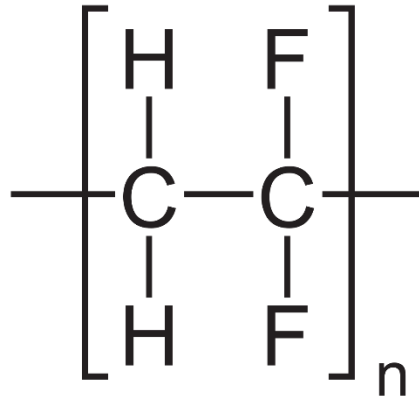


Figure 11. Chemical structure of PVDF [48].

PAN: The polyacrylonitrile (PAN) is $(C_3H_3N)_n$ and is a synthetic, semicrystalline organic polymer. Nearly PAN are resins copolymers, and they are made of monomers mixtures with acrylonitrile as the main monomer. This is thermoplastic polymer and higher melting point. It's melting point above 300 °C. The chemical structural formula of PAN is shown in Figure 12. The chemical formula of the PAN is $(C_3H_3N)_n$ [49].

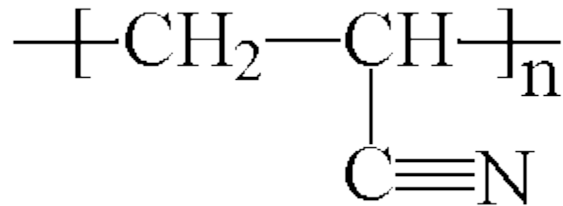


Figure 12. The chemical structure of polyacrylonitrile (PAN) [49].

7.1 Lamination of Nano fiber web

In order to prepare Nanofibrous multilayer membrane(s) we cut nanofiber(s) (A4 size (210*297 mm²) then 120 g/m² Polyethylene terephthalate(s) (PET) and adhesive web(s) (12g/m²) were used supporting layer. In the Heat-press machine (which is used to lamination samples) in Figure 13 and 14 there are two metallic plates (lower and upper) are used under pressure and nanofiber was kept in upper and adhesive web were kept in middle and spun bond nonwoven were kept down. Two silicon layers were used to protect direct contact between the multilayer nanofibrous membranes and the hot plates. By the hot upper and lower plate, the heat was applied 110⁰C and 125⁰C and 135⁰C for different sample duration of three minutes and two pressures were applied 30 KN in first two minute and 50 KN in rest one minute. For every temperature PVDF, PA6 and PAN nanofibers were used where PET and adhesive webs were fixed. The resultant multilayer nanofibrous membranes were name after the name of nanofiber area of nanofiber and temperature respectively, namely PVDF-1A-110, PA6-2A-125 and PAN-1.5A-135 (Table 2-5). For instance, PVDF-1A-110 stands for PVDF nanofiber which area is 1 gram per sq. meter and it's prepared by 110⁰C temperature. As our pressure was fixed same in every sample, we did not mention in sample name.

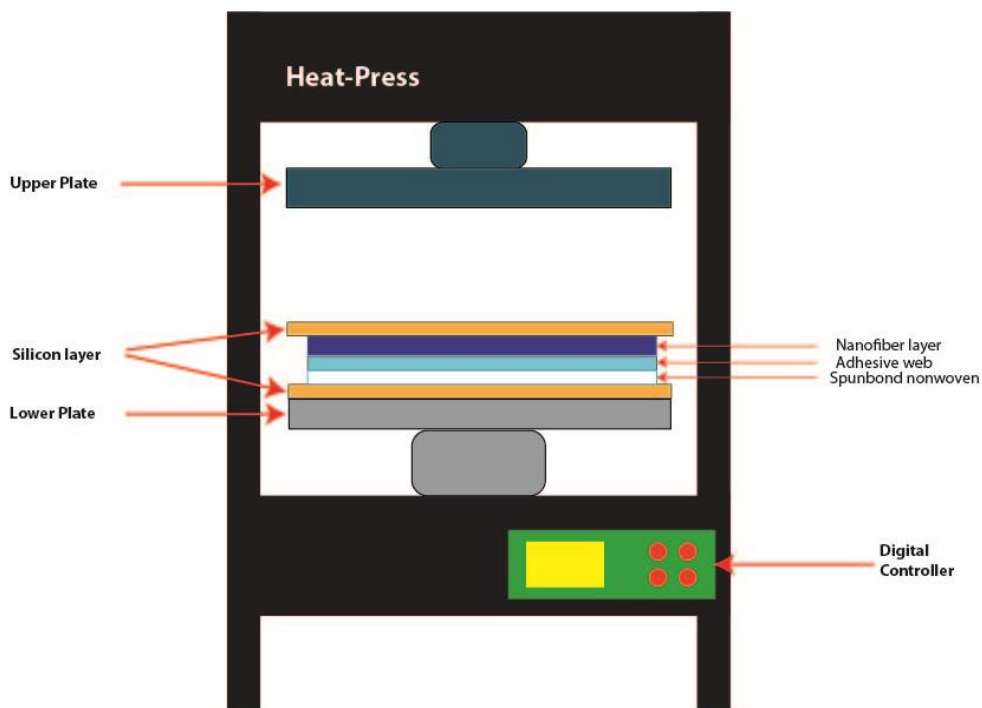


Figure 13. Schematic diagram of heat-press equipment and replacement of the multilayer nanofibrous membrane.

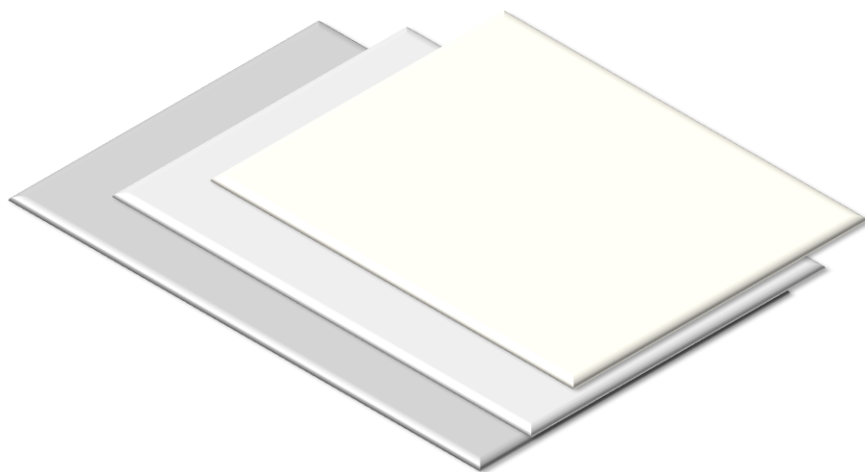


Figure 14. 3D Picture of Multilayer Membrane.

Based on the selectivity and water permeability results, selected nanofiber layer was laminated with different adhesive webs and supporting layer to observe the effect of adhesive web and supporting layer on nanofibrous membranes. These membranes are written in Tables 2, 3, and 4 with samples name and abbreviation.

7.2 Pore Size measurement

First, 7 cm² Sample was cut from nanofibrous membrane by cutter machine, then the sample was wet by GALDFILL liquid for about one minute. To, run Wirex machine first we on the airflow. After that, The Wirex software was connected to the computer and on the airflow pressure.

Next, the sample was kept on the sample holder and covers. Then we fixed the pore size 5.0 μm larger to small 0.2 μm and the pressure was 0.128 bar minimum to 3.2 bar maximum. Following that, we set the sample from wet to dry measurement. Finally, we run the device and got the maximum, minimum, and mean pore size values at least from 3 measurement of each sample. We collected the data and save them in an excel file.

7.3 Water flux Testing

An amicon stirring cell was used for the filtration test as shown in Figure 15. First, we cut a sample circular shape approx. 14 cm² and placed it to filtration device and close it. Then, fill the device with 40 ml of water and kept a test tube to measure the water. There is a tube of a device which is connected to the test tube to pass the water. The applied pressure was approximately 0.02 bar. After that, when water starts to drop into the test tube immediately stopwatch was counted and kept a record in minute(s) in 5 ml, 10 ml, 15 ml to in this sequence till 40ml.



Figure 15. Water flux testing machine.

The water flux and permeability has been calculated according to Equation 1 and 2;

$$F = \frac{1}{A} \frac{dV}{dt} \quad (1)$$

$$k = \frac{F}{p} \quad (2)$$

where V is the total volume of the permeate (L), A is the active membrane area (m²), t is the filtration time (hours) and p is the transmembrane pressure (bar).

7.4 Turbidity test for determination % removal of the micro-particles. (NTU Measurement)

We prepared a solution by polydispersed polystyrene particles (particle size about 0.503 μm) and mixed them into distilled water. Next, we took some solution on a test tube and vibrate the test tube with Ultrasonic Cleaner and put the test tube on Livobond Machine to measure the turbidity was approximately 134 NTU unit.

After that, we used the filtration unit to fill solution 40 ml, and the filtration unit is connected with silent Master Machine to pass the air pressure and with a test tube to measure solution and time. By silent master m/c we apply 0.002 bar pressure and count the time by the top watch in 5ml, 10 ml, 15 ml till 40 ml respectively. The solution came to the test tube we took and vibrate the solution by Ultrasonic cleaner. Again, we measure turbidity in NTU unit, and we get our desire result. Compare after and before NTU value we get our result (%) the separation efficiency has been calculated by using Equation 3.

$$E = \frac{C_2}{C_1} * 100 \quad (3)$$

where E is the particle separation efficiency (%), C1 is the NTU value of feed solution, C2 is the NTU value of permeate after separation.

7.5 Air permeability test

The digital air permeability tester (ATLAS 128 Air Permeability Tester (Rock Hill, SC, USA) set at 200 Pa and 20 cm²) precisely and swiftly determines the resistance of fabrics (woven, knitted, and non-woven textile materials) to the passage of air (airflow) under constant pre-set air pressure when firmly clamped in the test rig of the selected test head/area (Figure 16).



Figure 16. Air permeability tester

First, open the switch to enable the airflow of the machine. Then, the specimen is kept to the test area of the instrument easily with help of a clamping lever, 20cm² test head attached with the instrument. Next, by pressing down the clamping arm to start the test, this is a powerful and muffled vacuum which is a pump that draws air through with a circular opening. As air pressure is selected by standard so after few seconds air permeability is displayed on the screen with the unit. Again, pressing down the clamp removes the sample from the test area. At least 3 measurements were done for each sample.

7.6 Stress strain measurement

We took 3 portions of the fabric and measured stress and strain. The relationship between stress and stress can be represented by a material stress-strain curve. The load is gradually applied to a test coupon and deformation is measured to determine stress and strain. Taking into account a bar of the original sectional cross-section, F-pulling forces are equal to the opposite in order to stress the bar. The material has a stress defined as the force ratio and axial elongation of the transversal area of the bar.

$$\sigma = F / A_0 \dots \dots \dots \text{equation 4}$$

here, the σ stands for stress and F is force and A_0 is area.

$$\epsilon = \frac{\Delta L}{L_0} * 100 \dots \dots \dots \text{equation 5}$$

in the equation number 5, ϵ stands for ΔL is stress length and L is original length.

For ductile materials there will be a lot of tension required to start movement. As long as the distortion escapes the pinning, the stress is less. Normally the curve decreases marginally after the yield point. The first phase is the elastic linear region. The stress is proportional to the strain, it is the general rule of Hooke, and the slope obeys Young modulus. The material is only subjected to elastic deformation in this area. At the end of the point, the plastic deformation starts. This point is known as high yield point. The second step is the hardening field of strain. This region starts from the moment that the pressure exceeds the yield point to the maximum at the final force point. The necking area is the third level. In addition to the strength of the friction, a neck develops when the local intersection is much smaller than the average. The fracture ends in this region. The elongation of percent can be measured after fracture.

Apparently, the tensile properties of pristine nanofiber web increased enormously after lamination process. We investigated that all the tensile properties of the material is depends on the support layer used under nanofiber web. For this reason, all the mechanical strength results showed the same value due to the same nonwoven used. It was found that on machine direction 133 N/5cm, and on counter direction 107 N/5cm.

8. Result and discussion

8.1 pore size

The pore size of the membranes has a significant impact on permeability and flux and sometimes on effectiveness. The mean of the sample pore diameters is depicted in Table 5, Table 6 and Table 7, Figure 17.1, Figure 18.1 and Figure 19.1, the diameters are displayed. The results indicated that the pore size of the membranes are not depends on the lamination temperature. However, the pore size is very much depending on the type of nanofiber material. For instance, PA6 nanofibers have the lowest pore size while PVDF nanofibers have the biggest pore size. The reason could be due to fiber diameter. Smaller fiber diameter results in smaller pore size for nanofiber membranes.

8.2 Air permeability

In general, lower GSM is thought to result in better permeability. The major goal of measuring air permeability is to see how well the lamination process works. If the lamination process isn't done correctly, the glue can cover all of the nanofibers' pores. As a result, an air permeability test was performed on each membrane several times. The lamination process did not block the pores of the nanofiber web, according to air permeability results. In the Table 5, Table 6 and Table 7 and Figure 17.2, Figure 18.2 and Figure 19.2, we showed the air permeability PA6, PVDF and PAN respectively.

When we compared to air permeability, again the lamination temperature did not affect so much. On the other hand, density of the material and the type of the material has huge role on air permeability. Low density materials have less compact structure which increase in air permeability. Moreover, larger pore size membranes (such as PVDF), has higher air permeability compared to others due to large pores.

8.3. Water permeability

Water permeability during filtration can be caused by several factors such as membrane selectivity, type of polymeric materials, hydrophilicity, surface morphology, charge of membranes, pore size, etc.. While the liquid flows across the membrane, the solute is maintained at a relatively high concentration by the membrane's surface. During filtering, the hydrophilicity

of the membrane is further diminished due to membrane fouling and concentration polarization. Another cause could be membrane pore constriction or collapse. As a result, the permeability is reduced. Operating parameters such as feed pressure, temperature, pH, flow rate, and so on are important contributors in membrane permeability. In our thesis water permeability plays an important role as selectivity to choose best samples. In the Tables 5, 6, and 7, with Figure 17.3, Figure 18.3, and Figure 19.3 it was showed the permeability capacity of samples. We have tested water permeability with 40 ml water for each sample. In this 40 ml we start with stopwatch to measure how fast water is passing through the every sample.

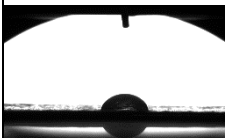





Compared to all polymeric membranes, PA6 showed the highest water permeability than others. The PVDF showed very low or zero permeability. The reason is PA6 has hydrophilic structure while PVDF is hydrophobic. Moreover, the micron size particles might capture within the large pores of PVDF and cause the membrane fouling.

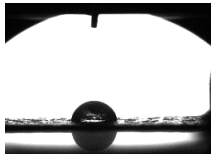
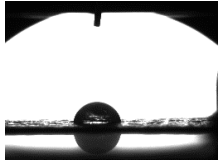


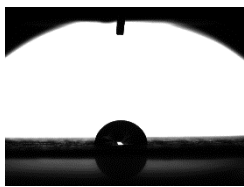
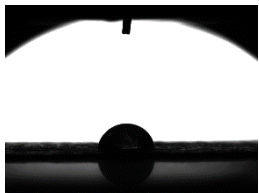
8.4. Contact Angle

Contact angle is a most important parameter of a sample, if the contact angle is high, it has possibility to less filtration capacity because of hydrophobic property. The surface roughness is related to the surface hydrophobicity. The surface of the web can be altered using heat and pressure. Furthermore, the adhesive web possesses hydrophilic properties that may affect the nanofiber web's surface. In our thesis we found most of the samples are hydrophilic after lamination, it might be due to adhesive web which is covering the nanofiber surface and reduce the hydrophilicity. However, PVDF for instance, some polymers are hydrophobic nature which can still affect the overall structure of hybrid membrane's permeability. In the Table 5, Table 6, and Table 7, with Figure 17.4, Figure 18.4, and Figure 19.4 it was showed the data statistics about our samples.

In the table 5, we have added the pore size, air permeability and water permeability results of PA6 nanofiber Membranes

Table 5. PA6 samples name with pore size and air permeability, water permeability(flux) and contact angle.

Name of Samples	Pore size (μm)	Average Air permeability ($\text{l/m}^2/\text{m}$)	Water permeability ($\text{L/m}^2.\text{hr}.\text{Bar}$)	Contact Angle(degree)	Image
PA6-1A-110	0.4348	4.035	2935.824	84 ± 4.3	
PA6-1.5A-110	0.3398	5.6	14737.20	83.5 ± 2.5	
PA6-2A-110	0.3622	5.1	9191.99	80.3 ± 3.5	
PA6-3A-110	0.4096	4.9	8075.496	90.2 ± 4.1	
PA6-1A-125	0.4261	4.8	5877.840	83.5 ± 3.5	
PA6-1.5A-125	0.4224	5.7	8450.020	83 ± 3.2	

PA6-2A-125	0.4002	4.5	4398.908	81±2.5	
PA6-3A-125	0.409	4.2	3749.284	82±3.4	
PA6-1A-135	0.4642	4.6	5343.982	81.45±3.8	
PA6-1.5A-135	0.5513	3.5	9211.613	80.45±3.7	
PA6-2A-135	0.3590	5.02	5226.602	82.2 ±3.6	
PA6-3A-135	0.364	4.8	2685.389	80.78±4.5	

Now we will the graph in column to compare the results pore size, air permeability, water permeability and contact angel respectively.

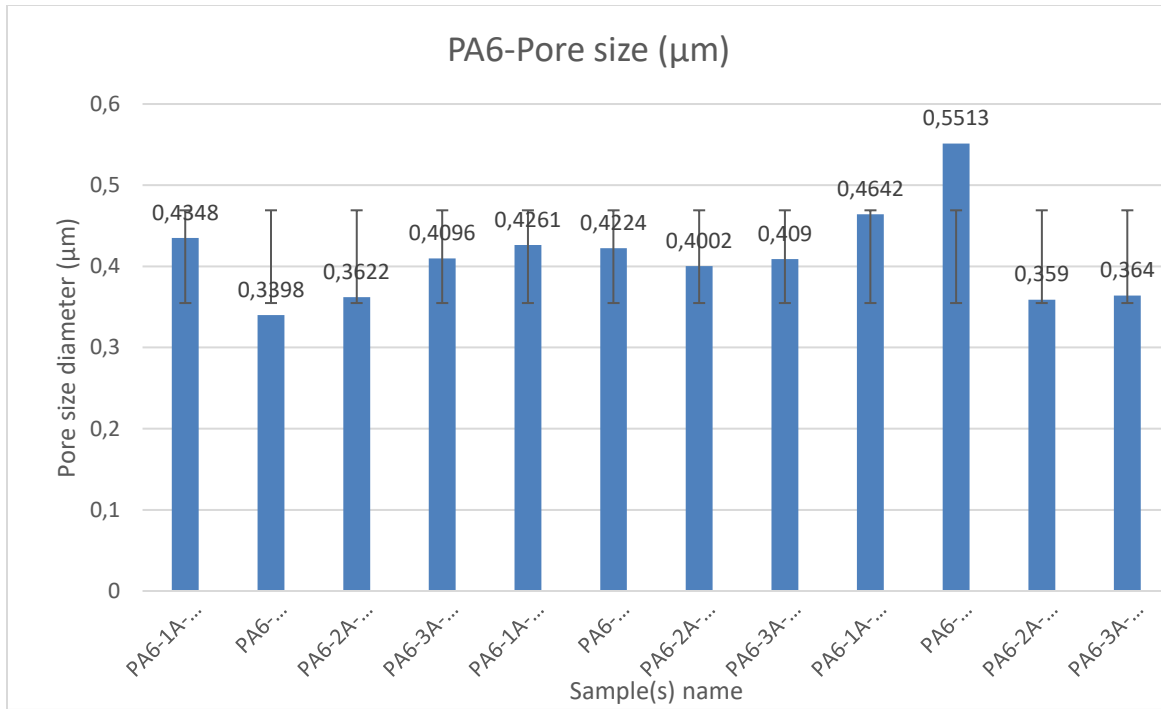


Figure 17.1. Pore size diameter of PA6 samples.

In the Figure 17.1 we can see that, pore diameter of all PA6 membrane is almost similar and no significant different among samples.

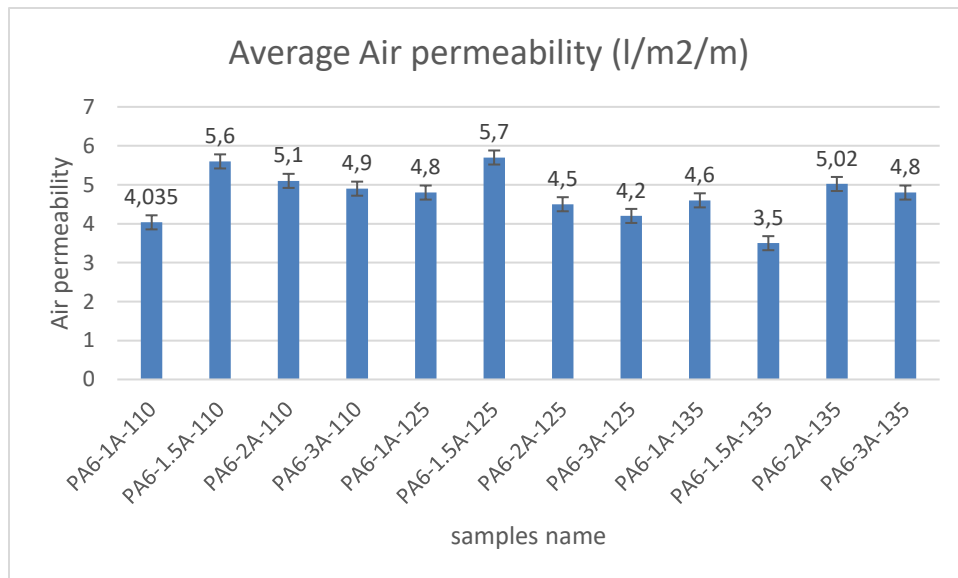


Figure 17.2. Air permeability of PA6 samples.

Air permeability is most important for separation micro-particles for air filters. In our case, we tested the air permeability for the lamination process. If there is almost zero permeability, it means adhesive is melt and cover all the pores. From the Figure 17.2 we can observe that, air permeability of samples is around 3.5 to 5.7 l/m²/min.

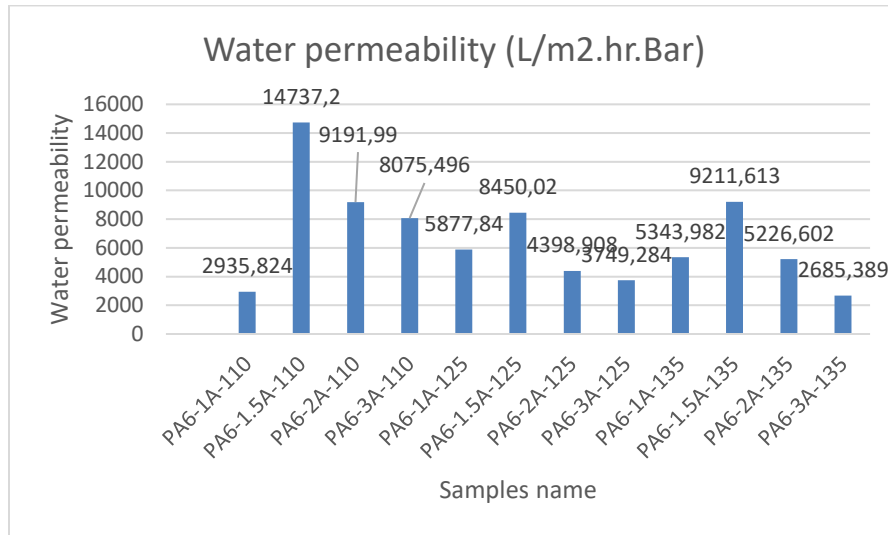


Figure 17.3. Water permeability (flux).

The Figure 17.3 illustrate that, PA6-1.5-110 is the best candidate to permeable water, taking into account other quality PA6-2A-110 and PA6-3A-110 are the better for water permeability test.

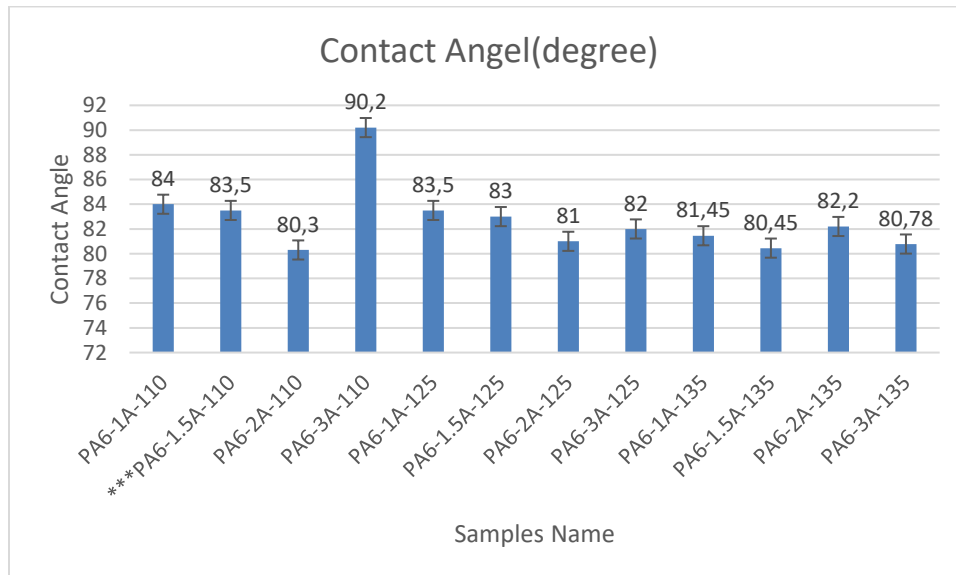


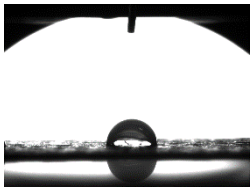
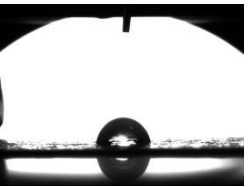
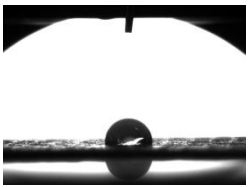
Figure 17.4. Contact angle of PA6 samples.

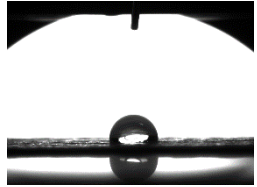
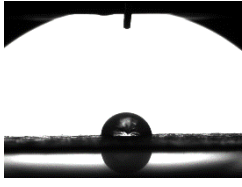
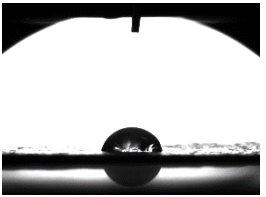
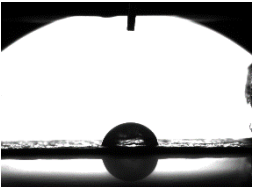
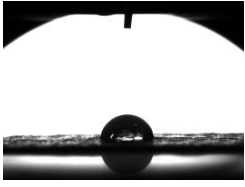
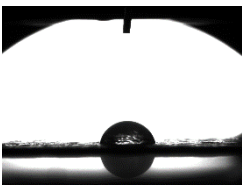
The Figure 17.4 illustrates contact angle of PA6 samples, here we can see that PA6-2A-110 is the least result compared to other samples.

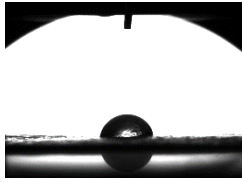
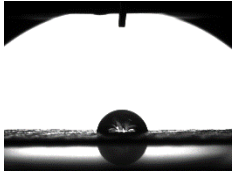
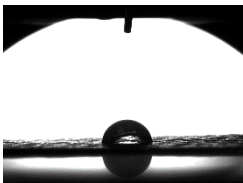
To sum up, from the table 04 we can say that three samples namely PA6-1.5-110, PA6-2A-110 and PA6-3A-110 are better candidate in narrow pore diameter, air permeability and water permeability test.

In the table 6, we have added the pore size, air permeability and water permeability results of PVDF nanofiber Membranes

Table 6. PVDF samples name with pore size and air permeability, water permeability (flux) and contact angle.

Name of Samples	PVDF-Pore size (μm)	Average Air permeability ($\text{l/m}^2/\text{m}$)	Water permeability ($\text{L/m}^2.\text{hr}.\text{Bar}$)	Contact angle(degree)	Image
PVDF-1A-110	0.8511	10.35	3027.888	80.23 ± 2.3	
PVD1.5A-110	0.696	5.32	983.412	86.5 ± 4.2	
PVDF-2A-110	0.5455	5.25	0	70 ± 9.5	

PVDF-3A-110	0.6511	4.65	2066.77	85±3.8	
PVDF-1A-125	0.785	9.53	3950.627	85±4.2	
PVDF-1.5A-125	1.1000	5.35	1858.493	78±6.23	
PVDF-2A-125	0.5510	4.235	2993.140	79.26±2.3	
PVDF-3A-125	0.5683	3.95	2896.038	74.5±6.2	
PVDF-1A-135	0.758	9.56	3003.614	86.2±5.2	

PVDF-1.5A-135	0.6427	5.6	2821.564	81.3±3.5	
PVDF-2A-135	0.5773	4.56	123.896	86.4±3.2	
PVDF-3A-135	0.6427	4.02	0	85.6±3.5	

Now we will the graph in column to compare the results pore size, air permeability, water permeability and contact angel respectively and we will select the best membrane from them.

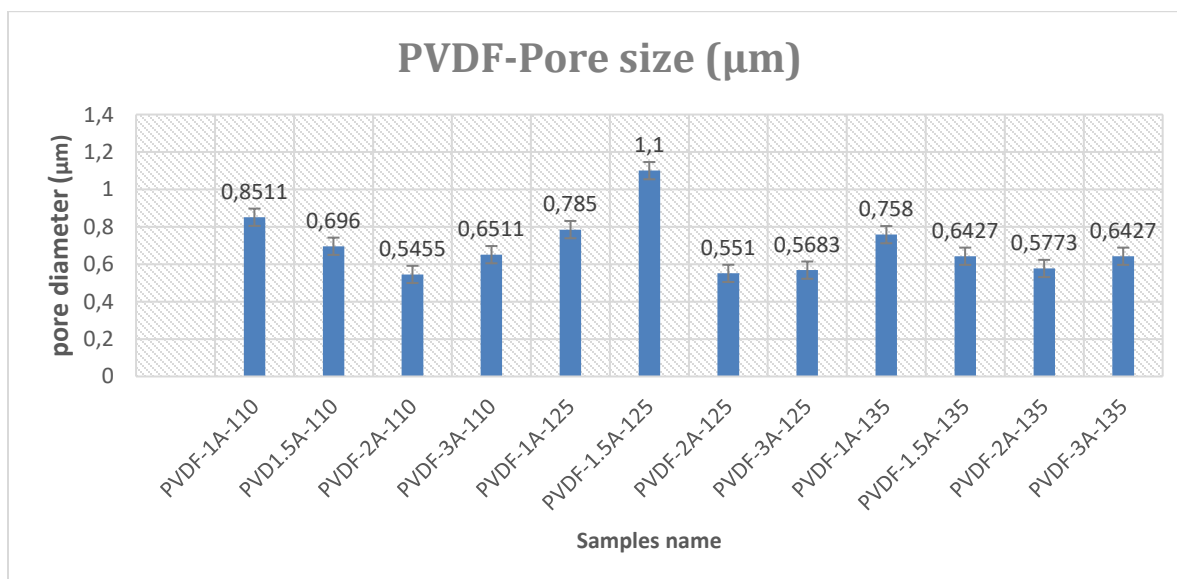


Figure 18.1. pore diameter of PVDF samples.

In the Figure 18.1 which is about pore size diameter of PVDF samples, we can see that almost all samples diameter is similar but PVDF-1.5A-125 is much bigger compare to other samples. To select the better sample(s) we will observe other test like water permeability and contact angles etc.

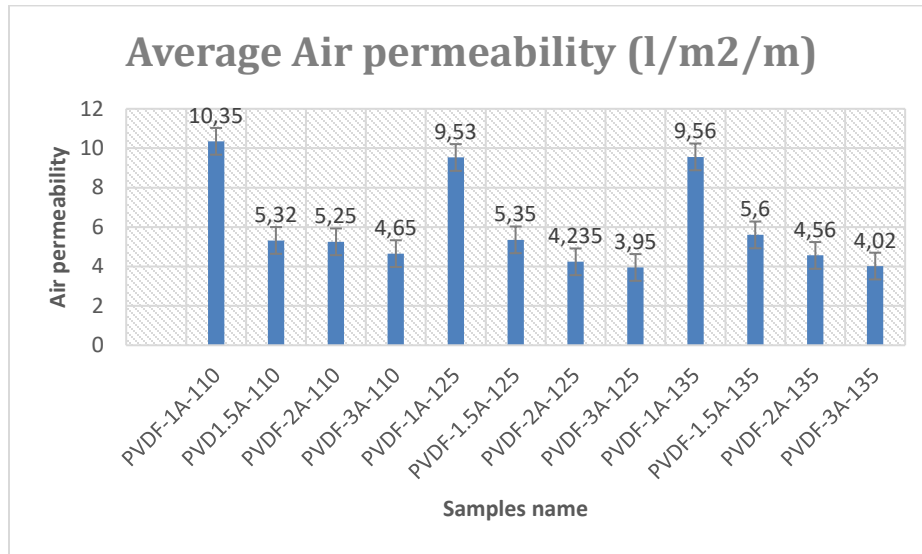


Figure 18.2. Air permeability of PVDF samples

From the Figure 18.2 we can say, PVDF-1A-110, PVDF-1A-125 and PVDF-1A-135 this three samples are almost twice air permeability compare to other samples. The molten adhesive which is filling the pores can cause unstable air permeability results among the samples and within the same sample.

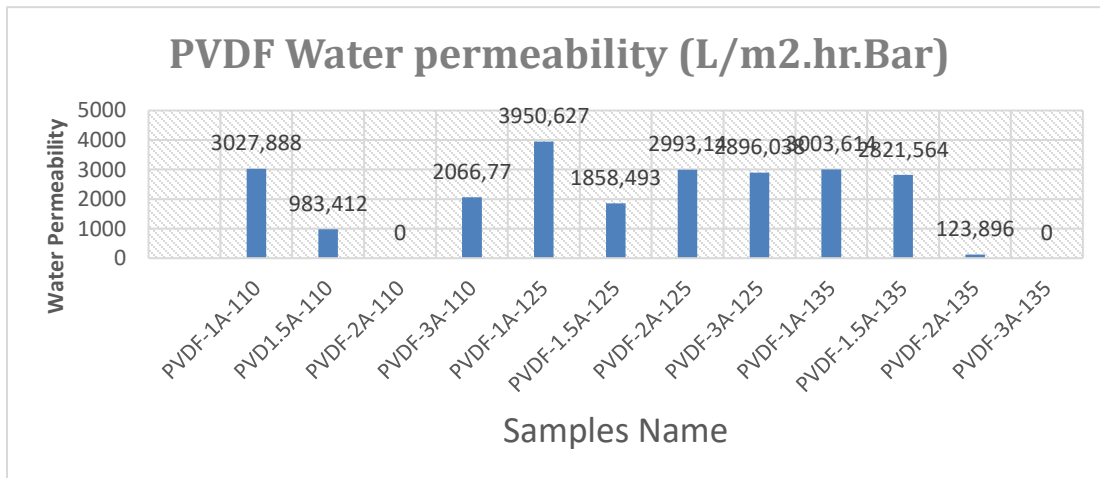


Figure 18.3. Water permeability of PVDF samples

In the Figure 18.3 we can say, the water permeability capacity is of those the samples namely PVDF-1A-110, PVDF-1A-125 and PVDF-1A-135 are the better than others samples, so we can say this three are better candidate from PVDF samples. However, overall result of PVDF showed these membranes has low performance compared to PA6 and PAN.

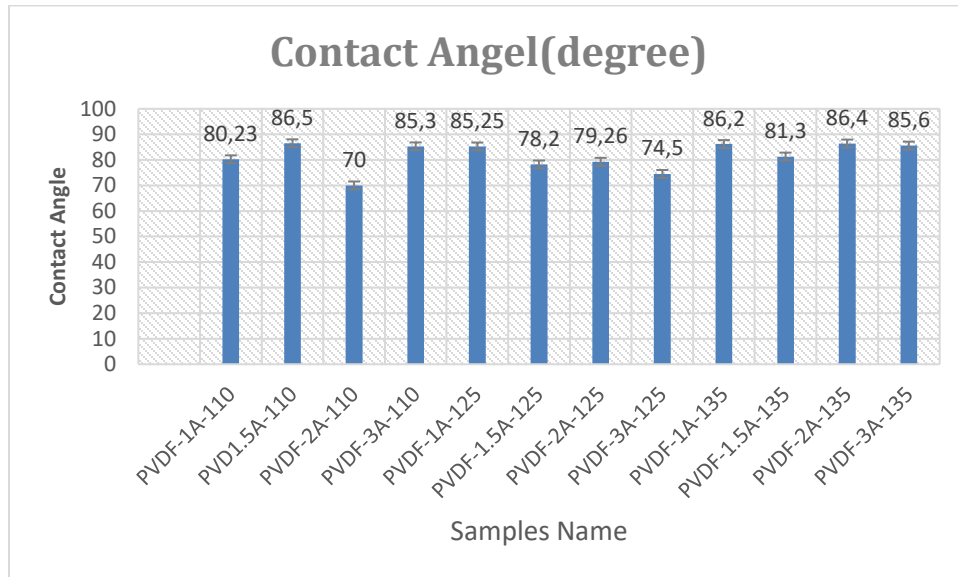
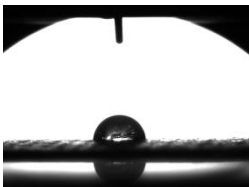
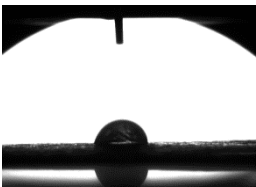

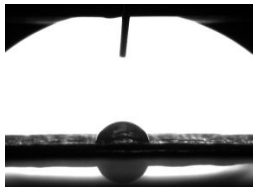
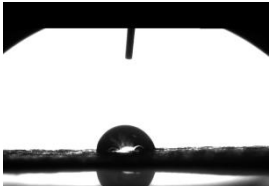


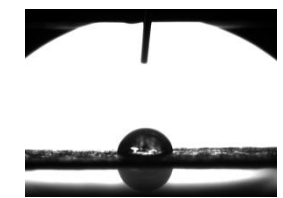
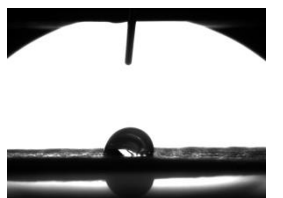
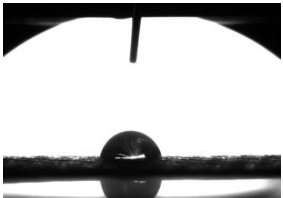
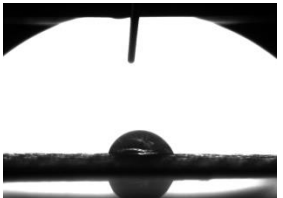
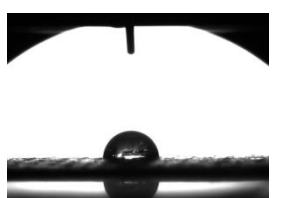
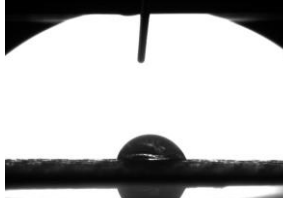
Figure 18.4. Contact angle of PVDF samples

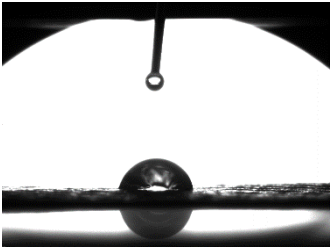
In the Figure 18.4 illustrates, PVDF are hydrophilic because their contact angle in less than 90 degree. Normally PVDF is hydrophobic, due to adhesive web, membrane shows hydrophilic structure on the top of the membranes.

PAN Nanofiber Membranes

Table 7. PAN samples name with pore size and air permeability, water permeability (flux) and contact angle.

Name of Samples	Pore size (μm)	Average Air permeability ($\text{l/m}^2/\text{m}$)	Water permeability ($\text{L/m}^2.\text{hr}.\text{Bar}$)	Contact angle (degree)	Image
PAN-1A-110	0.697933333 3	4.5	3363.61	87 \pm 2.8	
PAN-1.5A-110	0.425566666 7	4.8	3360.59	84.3 \pm 3.5	
PAN-2A-110	0.370933333 3	5.5	4368.83	75.5 \pm 3.4	
PAN-3A-110	0.4611	1.98	3136.140	78.5 \pm 4.2	
PAN-1A-125	0.637933333 3	7.31	8702.886	81.5 \pm 2.8	

PAN-1.5A-125	0.5118	5.98	6030.06	80.5±4.2	
PAN-2A-125	0.422466666 7	6.56	6441.14	82±3.6	
PAN-3A-125	0.4667	6.36	3978.15	84.5±2.5	
PAN-1A-135	0.7299	4.48	3698.32	74.8±4.5	
PAN-1.5A-135	0.425566666 7	5.55	5667.98	83.5±4.2	
PAN-2A-135	0.3757	4.68	3483.12	70.5±4.2	

PAN-3A-135	0.4498	3.98	4148.69	80.5±5.4	
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Now we will the graph in column to compare the results pore size, air permeability, water permeability and contact angel respectively and we will select the best membrane from them.

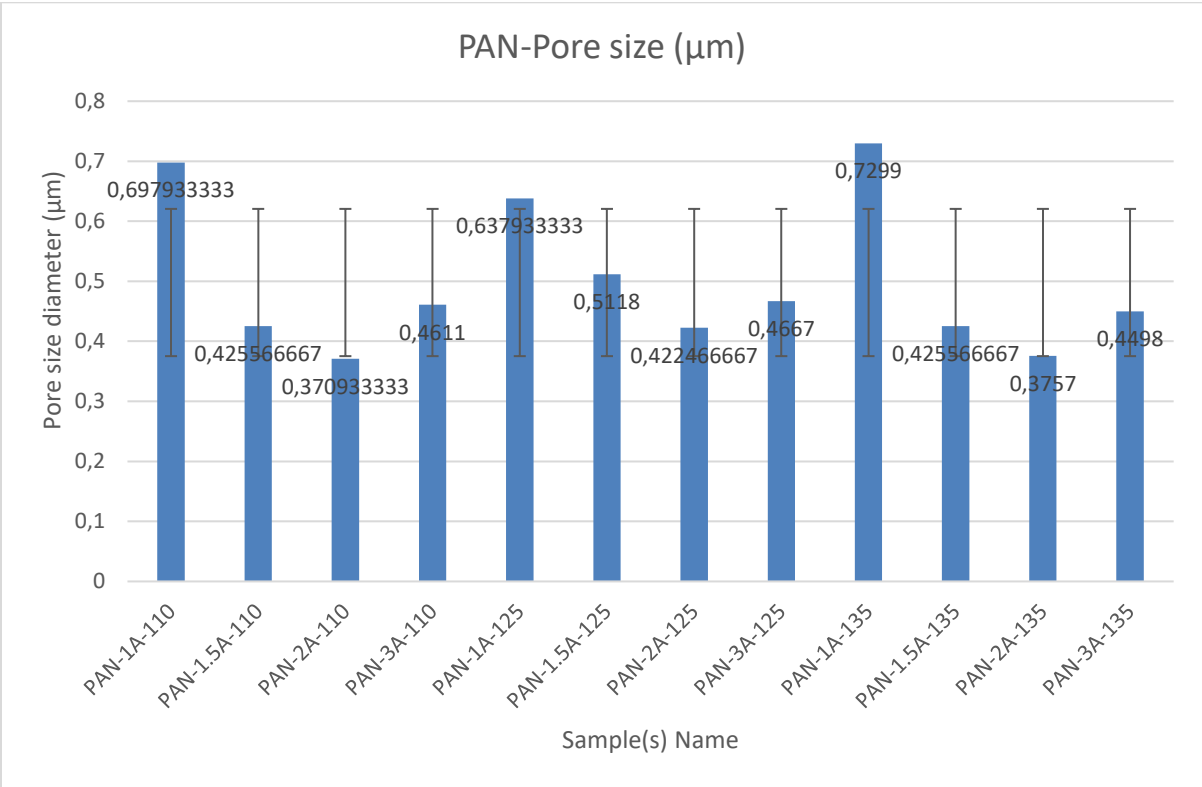


Figure 19.1. pore size measurement of PAN samples

From the data of figure 19.1 we can illustrate that, pore diameter of PAN-2A-110 is almost half compare with PAN-1A-135. There might be some droplets or holes on the membrane surface. It is difficult to produce defect free nanofibers. We cannot determine any sample from the pore diameter of the above samples

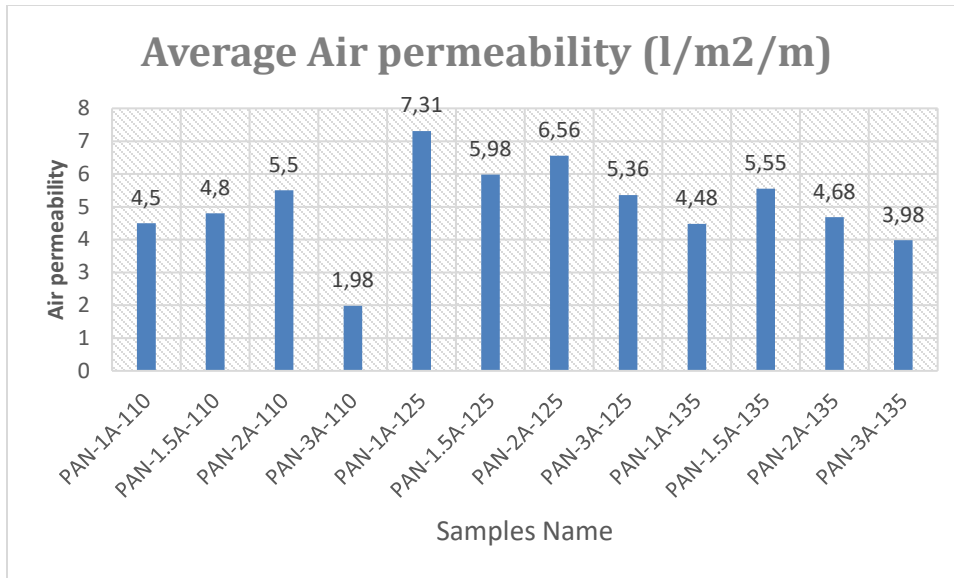


Figure 19.2. Air permeability of PAN samples.

The Figure 19.2 indicates, the air permeability of PAN-1A-125, PAN-1.5A-125 and PAN-2A-125 are more air permeable compared to other samples.

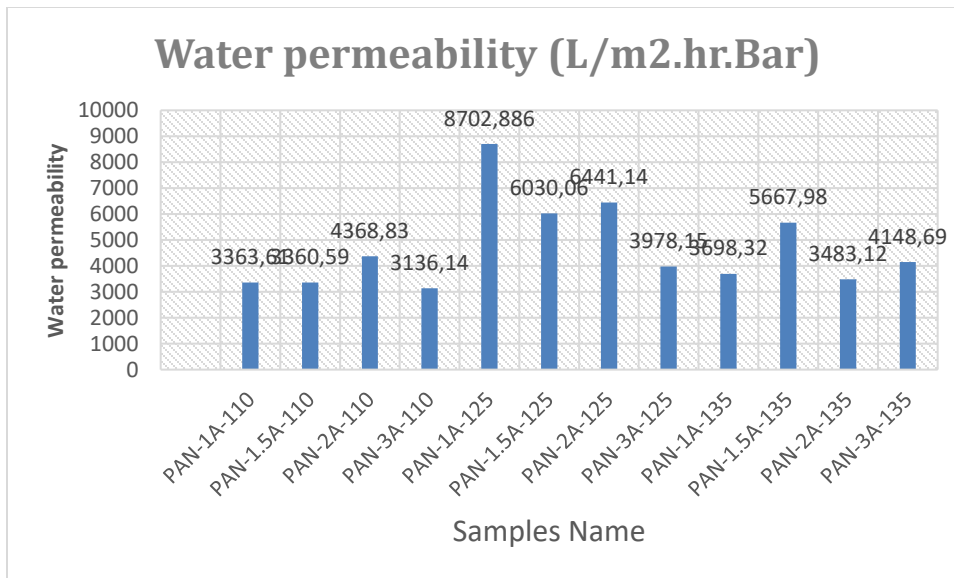


Figure 19.3. water permeability test results of PAN samples.

We can see on figure 19.3 on the base of water permeability PAN-1A-125, PAN-1.5A-125 and PAN-2A-125 are the better candidate compared to others.

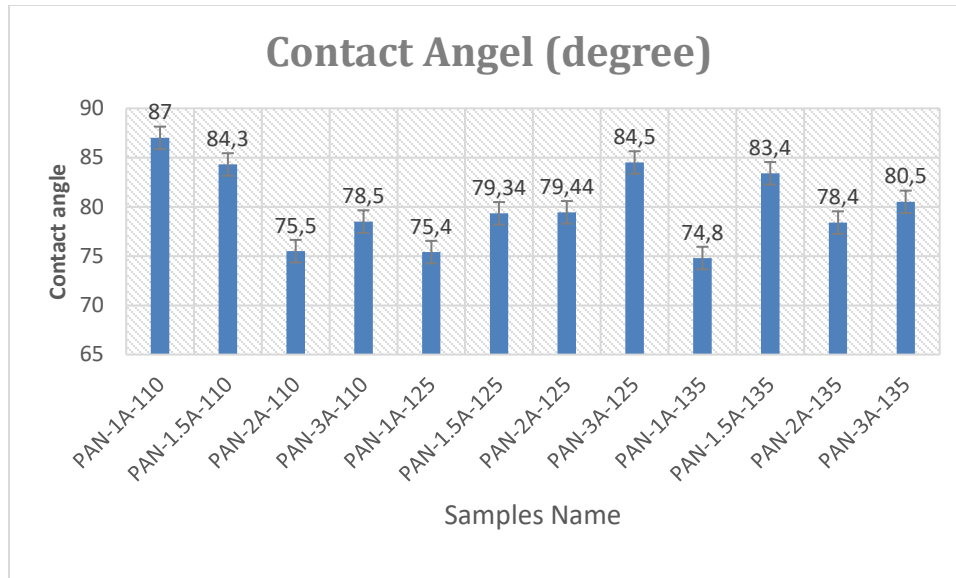


Figure 19.4. Contact angle results of PAN samples.

From the Figure 19.4 which is expressed the contact angle of PAN samples PAN-1A-125, PAN-1.5A-125 and PAN-2A-125 individually shows the less contact angle we can say they are hydrophilic.

8.5 Turbidity test (% removal of the micro-particles)

Turbidity refers to the amount of light that passes through a liquid sample. The amount of particles in suspension and their mean size are closely connected to the turbidity of slurries. It's a low-cost, easy method for detecting particles in suspension, and it's frequently used to quantify nucleation kinetics and metastable zone width. In the Technobis Crystal16 instrument, turbidity has also been used to test solubility (Simone and Nagy, 2015). Although not as exact as other measures, the level of turbidity can provide an indicator of the mean size and solid concentration of suspended particles [37]. Table 8, 9 and 10 show the % removal of particles from feed solution.

We have measured all samples turbidity (% removal of the micro-particles) which we have shown in Figure 21, Figure 22, and Figure 23 respectively samples of PA6, PVDF and PAN.

Table 8. Percentage of removal of micro particles of PA6 samples.

Name of Samples	% Removal of micro particles
PA6-1A-110	93.35
PA6-1.5A-110	98.58
PA6-2A-110	99.865
PA6-3A-110	99.9014
PA6-1A-125	92.4
PA6-1.5A-125	97.133
PA6-2A-125	96.37
PA6-3A-125	94.36
PA6-1A-135	97.08
PA6-1.5A-135	95.35
PA6-2A-135	97.69
PA6-3A-135	98.36

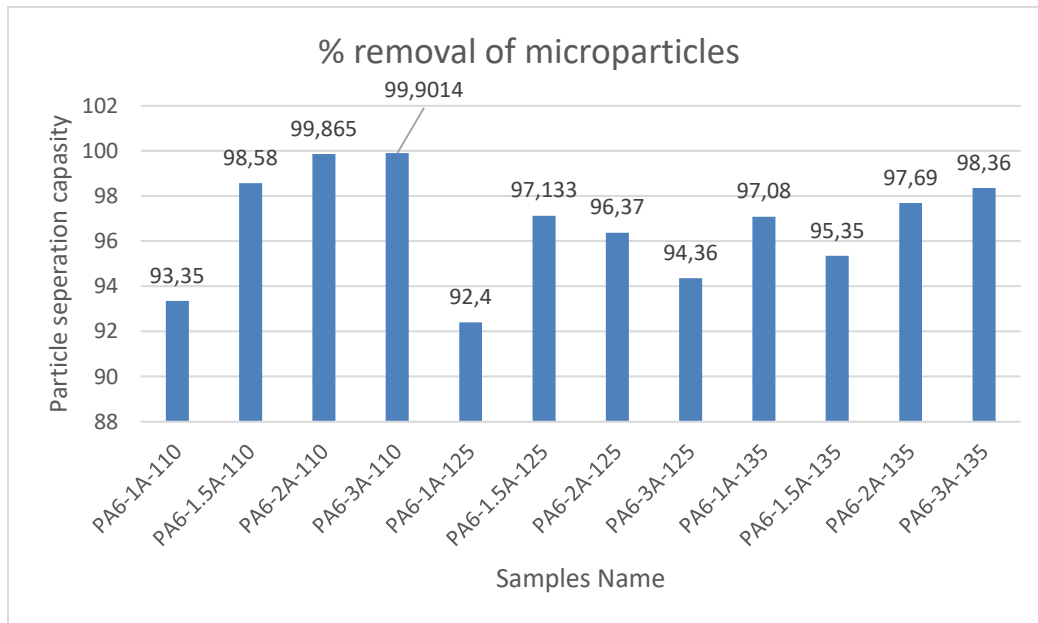


Figure 20. percentage of Removal of micro particles of PA6 samples

In the Figure 20 we can say, PA6-1.5A-110, PA6-2A-110 and PA6-3A-110 has better filtration capacity among the PA6 samples. These three samples individually 99 percentage effective in micro particle filtration due to their low pore size.

We will see the capacity of separation micro particles of PVDF samples, here provided table with graph of filtration capacity percentage.

Table 09. percentage of Removal of micro particles of PVDF samples.

Name of Samples	% Removal of micro particles
PVDF-1A-110	90.70
PVDF-1.5A-110	78.35
PVDF-2A-110	0
PVDF-3A-110	54.56
PVDF-1A-125	91.594
PVDF-1.5A-125	78.38
PVDF-2A-125	64.25
PVDF-3A-125	85.35
PVDF-1A-135	91.44
PVDF-1.5A-135	79.55
PVDF-2A-135	67.96
PVDF-3A-135	0

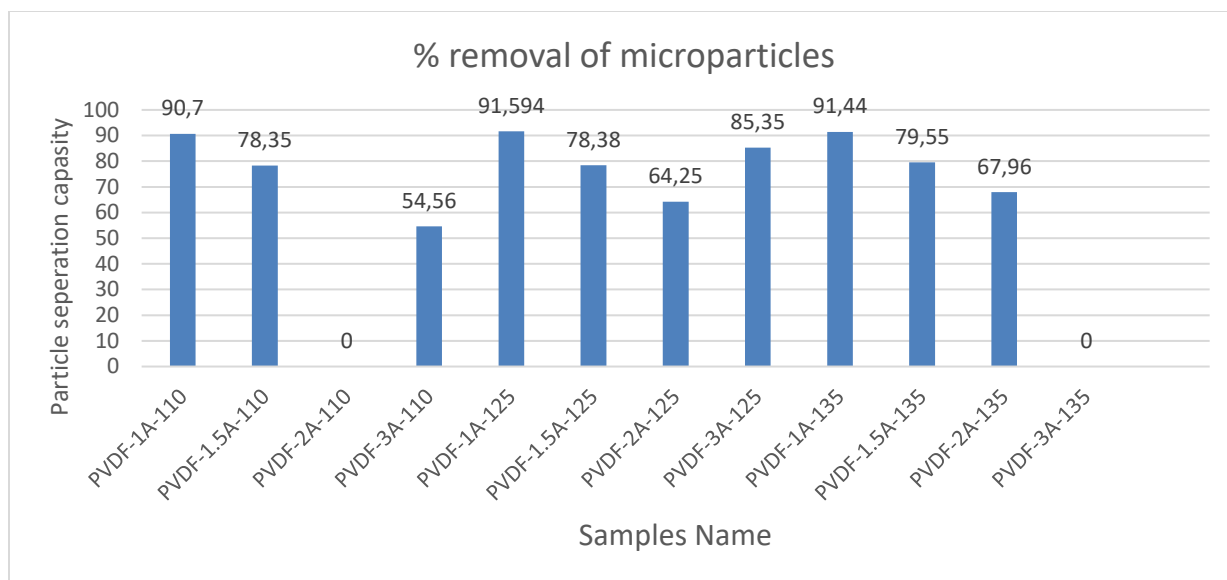


Figure 21. percentage of Removal of micro particles separation of PVDF samples.

In the Figure 21 illustrates, the percentage of Removal of micro particles of PVDF-1A-110, PVDF-1A-125 and PVDF-1A-135 these three samples are better candidate because their filtration capacity is better compared to other samples. However, when we compared to PA6, PVDF has very low particle separation. The main reason is their big pore size.

We will see the capacity of separation micro particles of PAN samples, here provided table with graph of filtration capacity percentage.

Table 10. percentage of Removal of micro particles of PAN samples

Name of Samples	% Removal of micro particles
PAN-1A-110	50.75
PAN-1.5A-110	68.68
PAN-2A-110	80.26
PAN-3A-110	72.26
PAN-1A-125	90.13
PAN-1.5A-125	90.7
PAN-2A-125	90.8
PAN-3A-125	74.5

PAN-1A-135	75.4
PAN-1.5A-135	65.9
PAN-2A-135	80.4
PAN-3A-135	85.4

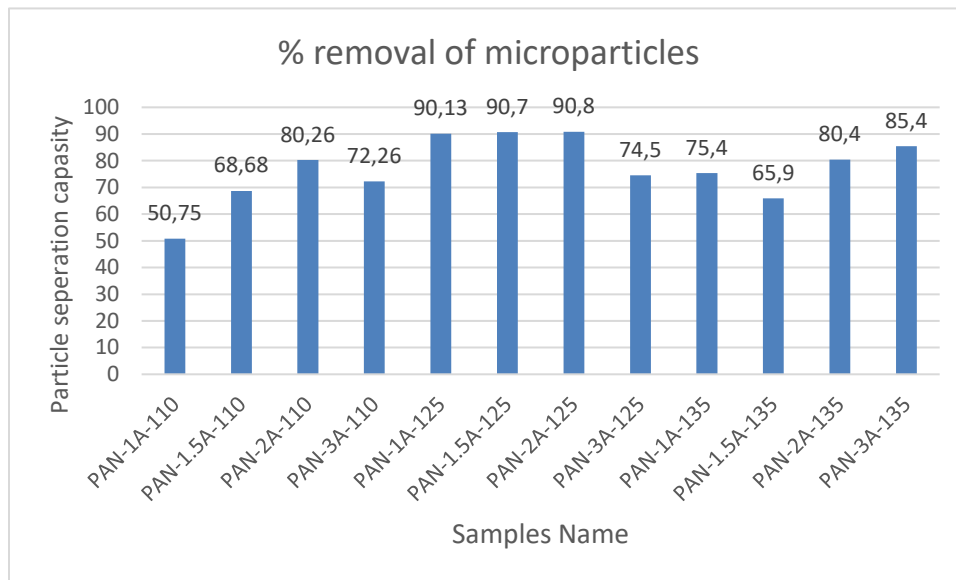


Figure 22. Percentage of removal micro particles

In the Figure 22 demonstrates, PAN-1A-125, PAN-1.5A-125 and PAN-2A-125 this samples individually shows the capacity above 90 percentage filtration capacity to filter micro particles. However, the separation efficiency performance was not as good as PA6 membranes.

To sum up, from the 36 samples, we have selected 3 samples individually from polyamide 6, PVDF and PAN.

In the basis of water permeability, air permeability and contact angle and capacity of filtration of micro-particles we have selected PA6-1.5A-110, PA6-2A-110 and PA6-3A-110, PVDF-1A-110, PVDF-1A-125 and PVDF-1A-135 and PAN-1A-125, PAN-1.5A-125 and PAN-2A-125 these nine samples are selected for final sample of our research.

8.6 Selected Membranes

We have performed several tests in term of performance about water permeability and micro particle separation we have selected some samples which we wrote on Table 11 below,

Table 11: Selected best candidate for filtration medium

Name of Selected samples	Filtration capacity (%)
PA6-1A-125	98.58
PA6-2A-110	99.865
PA6-3A-110	99.9014
PVDF-1A-110	90.7
PVDF-1A-125	91.594
PVDF-1A-135	91.44
PAN-1A-125	90.13
PAN-1.5A-125	90.7
PAN-2A-125	90.8

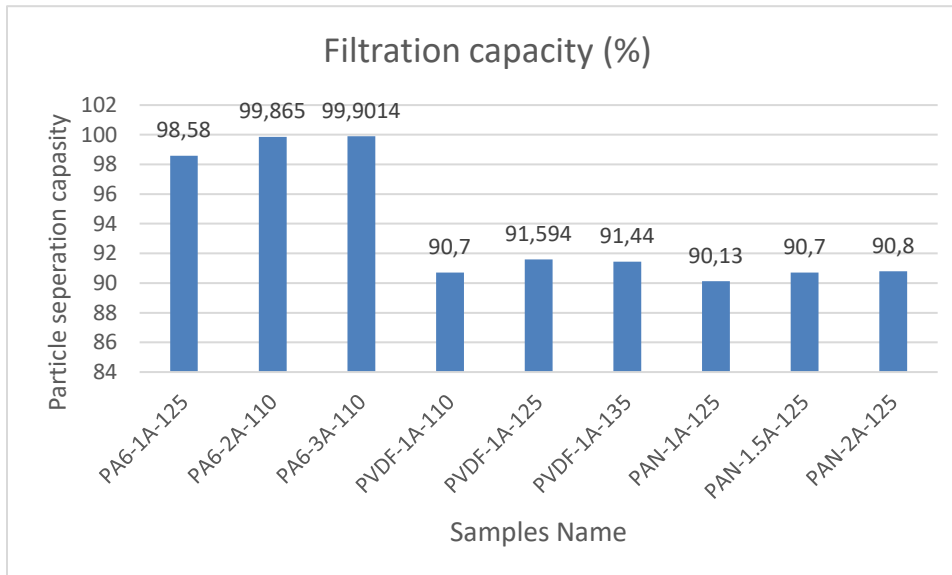


Figure 23. Filtration capacity of Selected candidate for filtration medium

Compare water permeability and filtration capacity with commercial membrane

We have compared our samples with some commercial membrane namely Fisherbrand, three category samples 1. Cellulose acetated pore size diameter 0.45 μm and thickness 47 mm.

2. Membrane filter nylon, pore size diameter 0.45 μm and thickness 47mm and 3. Membrane filter PES, pore size diameter 0.45 μm and thickness 47mm.

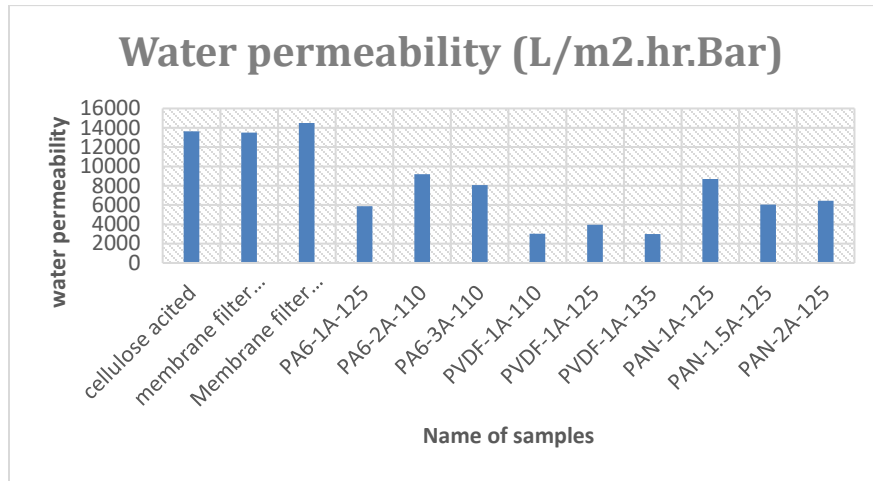


Figure 24: Comparable water permeability between commercial membrane and thesis samples

In the Figure 24, we can see that the water permeability of commercial membrane is almost double compared to our research samples, the thickness of commercial membrane is very low and its single nanofiber layer. In the next session we can see the particle separation capacity of above samples.

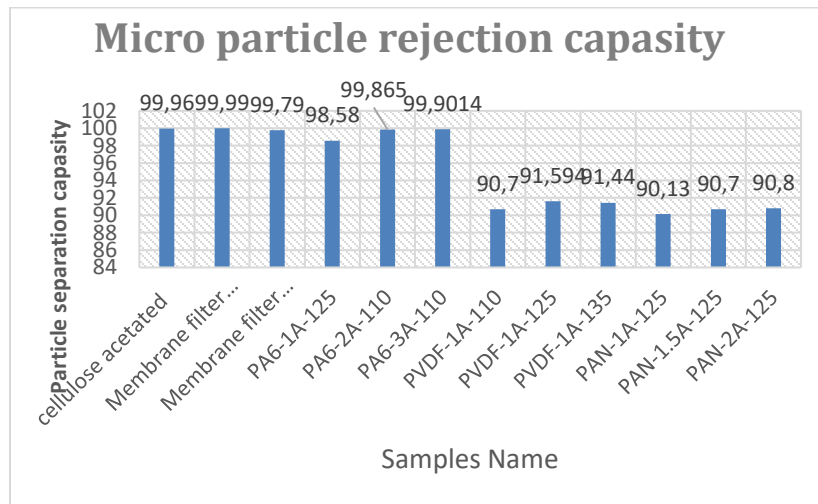


Figure 25. Compare selected samples and commercial membrane

From the Figure 25, its very clear that not all samples are effective like commercial samples, but some samples are effective in separation microparticles like commercial membrane, so we can say we invent some good filter by our research.

8.7 Surface morphology

Fiber surface morphology has taken by SEM images. In this morphology we have selected nine samples which we selected as best candidate from 36 samples. We can see that, the PA6 samples fiber diameter has less diameter compared to PVDF and PAN samples. PA6-2A-110 shows lowest fiber diameter and we saw our previous results PA6 samples are more effective in filtration process. Table 12. Fiber diameter of PA6 selected samples

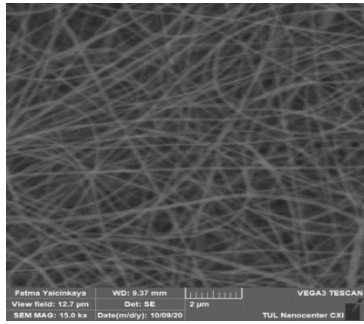
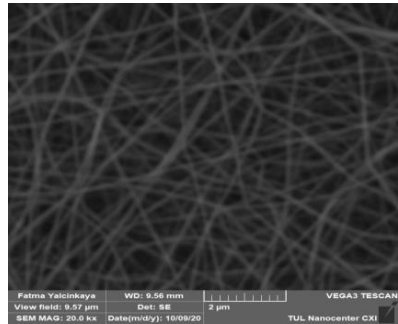
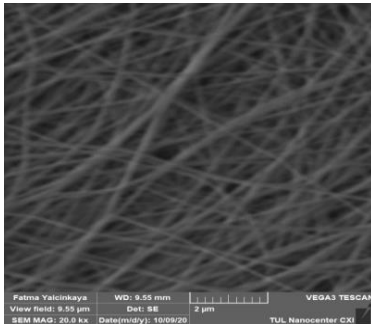
		
PA6-1.5A-125 Fiber diameter- 181 ± 7 nm	PA6-2A-110 Fiber diameter- 160 ± 5 nm	PA6-3A-110 Fiber diameter- 179 ± 6 nm

Table 13: Fiber diameter of PVDF selected samples

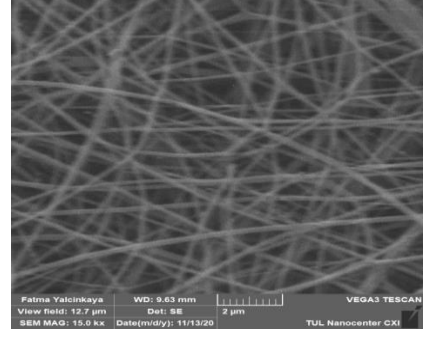
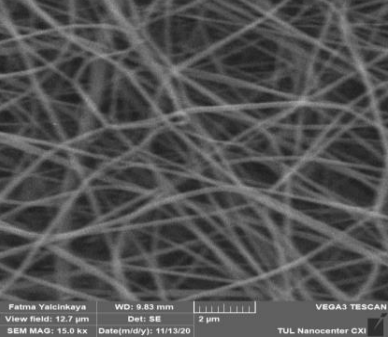
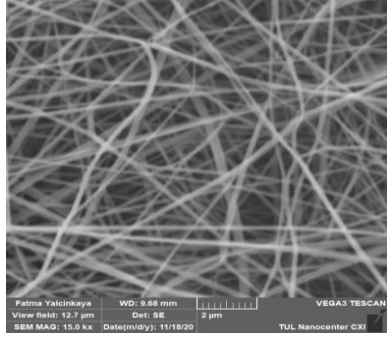
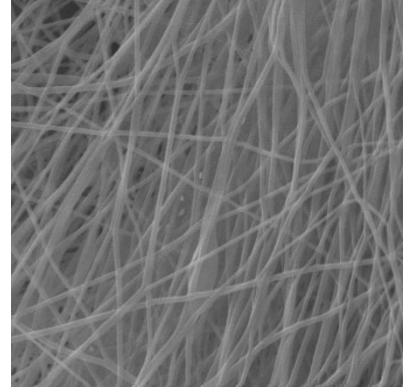
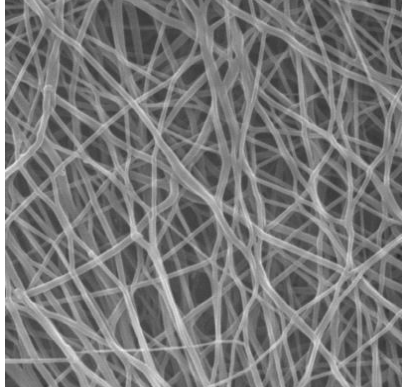
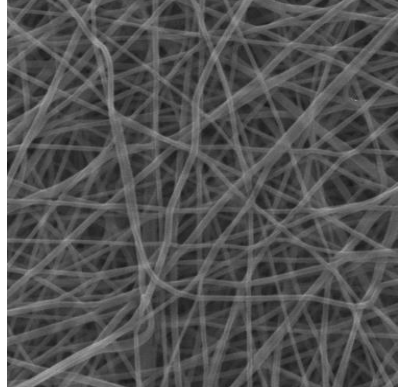
		
PVDF-1A-110 Fiber diameter- 213 ± 8 nm	PVDF-1A-125 Fiber diameter- 226 ± 9 nm	PVDF-1A-135 Fiber diameter- 190 ± 10 nm

Table 14: Fiber diameter of PAN selected samples

 <p>Fatma Yalcinkaya WD: 8.83 mm VEGA3 TESCAN View field: 12.7 µm Det: SE 2 µm SEM MAG: 15.0 kx Date(m/d/y): 08/27/20 TUL Nanocenter CXI</p>	 <p>Fatma Yalcinkaya WD: 9.01 mm VEGA3 TESCAN View field: 12.7 µm Det: SE 2 µm SEM MAG: 15.0 kx Date(m/d/y): 08/27/20 TUL Nanocenter CXI</p>	 <p>Fatma Yalcinkaya WD: 8.83 mm VEGA3 TESCAN View field: 12.7 µm Det: SE 2 µm SEM MAG: 15.0 kx Date(m/d/y): 08/27/20 TUL Nanocenter CXI</p>
<p>PAN-1A-125 Fiber diameter- 197±6 nm</p>	<p>PAN-1.5A-125 Fiber diameter- 208± nm</p>	<p>PAN-2A-125 Fiber diameter- 191±6 nm</p>

To sum up from table 12, table 13 and table 14 we can see that, the fiber diameter of PA6 samples is less compared to PVDF and PAN. We also get good filtration capacity from PA6 membrane, so for our experiment purpose we also make some new sample by using PA6 nanofiber membrane with changing the base layer and adhesive web and we get good filtration capacity which we include samples abbreviation on Table 2, 3 and 4 and our appendix.

9. Conclusion

In our research we have found result pore size, air, and selectivity, contact angle, strength, of nanofibrous membranes were all examined in this thesis. Different densities of PVDF, PAN, PA6 nanofibrous membranes were examined (GSM). It is found that the temperature and pressure has not good impact on result of filtration. It was discovered that the less pore size samples are more effective as a filtration membrane. In this case PA6 samples are good in filtration it has narrow pore size and small fiber diameter.

In our thesis we find some PVDF samples shows some hydrophobic property, and the membrane does not adsorb the water and did not get any water permeability. Though PAN samples have good permeability, but we did not get good micro filtration capacity compared to PA6 samples.

In our research we have seen that the PA6 nanofiber membrane are more appropriate to prepare microfilter.

As a future work, it is planned to continue

- make PVDF modification to absorb water

- measurement of the long-term efficiency of membranes

- measurement the self-cleaning property of membrane

- effect of heat and pressure on membrane

- we will change the supporting layer to see the effect of adhesive web and membrane effectiveness.

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