ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

FABRICATION OF THIN FILM NANOCOMPOSITE PRESSURE RETARDED OSMOSIS (PRO) MEMBRANES USING CELLULOSE NANOCRYSTAL (CNC) AND EVALUATION OF PERFORMANCES IN THE PROCESSES

Ph.D. THESIS

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

SELÜLOZ NANOKRİSTAL KULLANILARAK İNCE FİLM NANOKOMPOZİT BASINÇ GECİKTİRMELİ OSMOZ (BGO) MEMBRANLARININ ÜRETİMİ VE PROSESLERDE PERFORMANS TESTLERİNİN GERÇEKLEŞTİRİLMESİ

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ŞUBAT 2021

Mehmet Emin Paşaoğlu, a Ph.D. student of ITU Graduate School student ID 501142701, successfully defended the thesis/dissertation entitled "FABRICATION OF THIN FILM NANOCOMPOSITE PRESSURE RETARDED OSMOSIS (PRO) MEMBRANES USING CELLULOSE NANOCRYSTAL (CNC) AND PERFORMANCES IN PROCESSES", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İsmail KOYUNCU** Istanbul Technical University	.....
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Date of Submission : 19 January 2021
Date of Defense : 2 February 2021

To my family and my lovely son,

FOREWORD

I would like to express my deepest gratitude to my supervisor Prof. Dr. Ismail KOYUNCU for having faith in me to complete this comprehensive thesis. Without his support and encouragement, this research would not have been possible. He guided me and gave me the opportunity to conduct my research in National Research Center on Membrane Technologies (MEM-TEK).

I would like to thank ITU Scientific Research Council (BAP) for their financial support under grant (Project No:MGA-2017-40885).

I would also like to thank National Research Center on Membrane Technologies (MEM-TEK) where I have very good time and experience for the last eight years. In this context, I would like to thank each and every MEM-TEK members especially Dr. Recep KAYA, Dr. Türker TÜRKEN and Dr. Reyhan ŞENGÜR-TAŞDEMİR.

Great appreciation goes to jury members, Prof. Dr. Bülent KESKİNLER and Assoc. Prof. Dr. Derya Yüksel KÖSEOĞLU-İMER for their valuable comments about my thesis. Without them, I could not improve my thesis this far.

A special thanks to Assoc. Prof. Dr. Mustafa Evren ERŞAHİN and Dr. Caner ÜNLÜ for their valuable guidance and productive discussions for being an elder brother.

Most importantly, I'm indebted to my family members Ahmet Nuri and Avniye PAŞAOĞLU who always proud of me, support my decisions whatever the consequences; Ayşe PAŞAOĞLU and the deceased Mustafa PAŞAOĞLU who support me at every step of my life; Rabia Rümeysa and Enes PAŞAOĞLU who are beloved ones; Mustafa PAŞAOĞLU who is the source of pride of me; Ayşenur and Esmanur PAŞAOĞLU for the laughter we share.

December 2020

Mehmet Emin PAŞAOĞLU
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ABBREVIATIONS

AFM : Atomic Force Microscopy
AGUs : Anhydroglucopyranosis Units
ANC : Amorphous Nanocrystal
BNC : Bacterial Nanocellulose
BPF : Bamboo Pulp Fiber
CA : Cellulose Acetate
CE : Counter Electrode
CFS : Confined Feed System
CGS : Centimeter Gram Second
CMG : Carboxymethyl Guar
CNC : Crystal Nanocellulose
CNF : Carbon Nanofiber
CNT : Carbon Nanotube
CTA : Cellulose Triacetate
DC : Direct Current
DI : Deionized
DMA : Dynamic Mechanical Analysis
DMAc : Dimethylacetamide
DMF : Dimethylformamide
DP : Degree of Polymerization
DS : Draw Solution
DSC : Differantial Scanning Calorimeter
DSSCs : Dye Sensitized Solar Cells
EC : Electrical Conductivity
EDLCs : Electrical Double Layer Capacitors
EVA : Ethylene Vinyl Acetate
FESEM : Field Emission Scanning Electron Microscopy
FO : Forward Osmosis
FS : Feed Solution
FTIR : Fourier Transform Infrared Spectroscopy
HDPE : High Density Polyethylene
IP : Interfacial Polymerization
MF : Melamine Formaldehyde
MFC : Microfibrillated Cellulose
MNE : Multiple Needle Electrospinning
MPD : M-Phenylenediamine
MWC : Meter Water Column
NC : Nanocellulose
NCC : Nanocrystalline Cellulose
NF : Nanofiber
NFC : Nanofibrillated Cellulose
OEM : Original Equipment Manufacturer
OTR : Oxygen Transmission Rate
PA : Polyamide

PAH : Polycyclic Aromatic Hydrocarbons
PAN : Polyarcylonitrile
PB : Polybutadiene
PBI : Polybenzimidazole
PCs : Pseudo Capacitors
PE : Polyethylene
PEO : Polyethylene Oxide
PES : Polyethersulfone
PET : Poly(ethylene terephthalate)
PHAs/PHBs : Polyhydroxyalkanoates
PI : Polyimide
PLA : Polylactides
PMMA : Poly(methylmethacrylate)
PPy : Polypyrrole
PRO : Pressure Retarded Osmosis
PS : Polystyrene
PSf : Polysulfone
PVA : Polyvinyl Alcohol
PVDF : Poly(vinylidenefluoride)
PVDF : Poly(vinylidenefluoride)
PVOH : Polyvinyl Alcohol
PVP : Polyvinylpyrrolidone
SAXC : Small Angle X-Ray Scattering
SDS : Sodium Dodecyl Sulfate
SEM : Scanning Electron Microscopy
SGE : Salinity Gradient Energy
sPSU : Sulfonated Polysulfone
TEM : Transmission Electron Microscopy
TFC : Thin Film Composite
TFN : Thin Film Nanocomposite
THF : Tetrohydrofuran
TMC : 1,3,5-Benzenetricarbonyl trichloride
UFS : Unconfined Feed System
WAXD : Wide Angle X-Ray Diffraction

SYMBOLS

ne	**:** Entanglement Number
Mw	**:** Molecular Weight
Me	**:** Solution Entanglement Molecular Weight
ϕp	**:** Polymer Volume Fraction
µL	**:** Microlitre
Jw	**:** Water Flux
Js	**:** Salt Flux
Da	**:** Dalton
wt	**:** Weight

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FABRICATION OF THIN FILM NANOCOMPOSITE PRESSURE RETARDED OSMOSIS (PRO) MEMBRANES USING CELLULOSE NANOCRYSTAL (CNC) AND EVALUATION OF PERFORMANCES IN THE PROCESSES

SUMMARY

Nowadays, owing to quick world population growth and abrupt economy, high water demands desire innovative technologies in order to ensure clean and safe water with lower energy use. Severe environmental emissions arising by the consumption of fossil fuels often needs us to build energy harvesting technology which are environmentally sustainable. As an advanced technology, osmotic membrane processes consisting of forward and pressure-retarded osmosis, are conceived to be conspicuous technologies for the treatment, recycling and reuse of wastewaters and the harvesting of salinity gradient energy which is called "Blue Energy". Nevertheless, forward osmosis (FO) and pressure retarded osmosis (PRO) are at the level of growth yet. It is difficult piece of work to fabricate osmotic membranes obtaine high water permeability and perfect ion retention. The ideal osmotic membrane candidate can be a thin film composite membrane satisfy the conditions which has high water permeation and as soon as low reverse salt flux ratio. Furthermore, for the membrane to endure relatively high hydraulic pressures in PRO systems, certain mechanical properties are vital. Thankfully, membranes that are fabricated with electrospinning method have an excellent capability to overcome all specifications of the perfect support layer in consequence of porous structure characteristics and simplicity with that nanomaterials may be integrated to enhance the nanofibers mechanical strength. Apart from this, interfacial polymerization (IP) may be accomplished to electrospun nanofiber membrane to achieve a very thin selective polyamide coating. TFN membranes may show tremendous potential in osmotically driven membrane processes after integrating nano additives into their support layer.

The aim of this thesis to carry out and design a comprehensive study on the development of reinforced pressure retarded osmosis membranes. Specifically, this thesis presents the development of novel nanofiber supported thin film composite membranes with high water permeability and excellent selectivity for solvents, while showing an excellent mechanical strength for PRO processes. Interfacial polymerization reactions were used to construct very thin polyamide selective layer on the support, and electrospinning process was used to fabricate a number of support layers.

Initially, we investigated the potential to use flat sheet electrospun polyacrylonitrile nanofibers as support support layer to fabricate PRO membranes. Polyamide TFCs were successfully applied on five different substrate containing 0,1,2,5,10% crystal nanocellulose (CNC) in 16% PAN polymer solution. PRO membranes successfully fabricated via tailor-made flat sheet fabrication unit. It is concluded that PAN and CNC generated a complete mixture according to SEM, FTIR, DMA & contact angle analysis findings.The addition of CNC improved the mechanical strength of PAN support

layers which is the main phenomenon in PRO applications. The newly developed membrane can achieve a higher PRO water flux of 300 LMH, using a 1 M NaCl draw solution and deionized water feed solution. The corresponding salt flux is only 1.5 gMH. The reverse flux selectivity represented by the ratio of water flux to reverse salt flux (*Jw*/*Js*) was able to be kept as high as 200 L/g for PRO operation.

Following the success of flat-sheet TFN PRO membrane fabrication, improvements need to be done to increase packing density of fabricated final membrane modules. In this point, we used a novel technique to fabricate tubular membranes for PRO applications. The newly fabricated membrane achieves a higher PRO water flux of 405.38 LMH with using a 1 M NaCl and a DI as feed water. The corresponding salt flux is found as 2.10 gMH which is higher than flat sheet membranes. The selectivity of the reversed flux represented by the ratio of the water flow to the reversed salt flux (Jw/ Js) was able to be kept as high as 193.03 L/g for PRO operation.As far as we know, the performance of the work developed membrane in this study has shown better performance than all PRO membranes reported in the literature previously.

SELÜLOZ NANOKRİSTAL KULLANILARAK İNCE FİLM NANOKOMPOZİT BASINÇ GECİKTİRMELİ OSMOZ (BGO) MEMBRANLARININ ÜRETİMİ VE PROSESLERDE PERFORMANS TESTLERİNİN GERÇEKLEŞTİRİLMESİ

ÖZET

Günümüzde hızlı küresel nüfus artışı karşısında artan yüksek su ihtiyacı sonucunda daha az enerji tüketimi ile temiz su sağlayan yenilikçi teknolojilerin geliştirilmesi gerekmektedir. Fosil yakıtların kullanımından kaynaklanan ciddi çevresel emisyonlar, genellikle südürülebilir enerji üretimi yapabilen teknolojileri oluşturmamıza ihtiyaç duyar. Aslında, küresel enerji talebi esas olarak fosil yakıtlara dayalı 1971'den bu yana iki katından fazla artmıştır. Bu nedenle dünyamız, fosil yakıt rezervlerindeki azalma ve iklim değişikliğine neden olan sera gazları emisyonları nedeniyle enerji tedariki için benzeri görülmemiş zorluklarla yakın gelecekte karşıya kalacaktır. Bu problemin oluşturabileceği etkileri azaltmak amacıyla, fosil yakıtların kullanımını büyük ölçüde azaltmak için, uygun fiyatlı, temiz, güvenli ve yeterli enerji kaynakları sağlamak, dünyanın en büyük zorluklarından biri olmaya devam edecektir. Bu nedenle, dünya enerji talebinin karışlanması ve fosil enerji kaynaklarının kullanımının aşamalı olarak azaltılması için yenilenebilir enerji kaynaklarına olan ihtiyaç son yıllarda artmıştır. Bu nedenle, birçok araştırmacı bu talebi karışlamak için alternatif enerji kaynaklarına odaklanmaktadır, bunlar: güneş, rüzgar, med-cezir, dalga ve biyokütle kapsamlı çalışmalardır. Yine de, enerji kaynaklarının dengesiz mevcudiyeti, karmaşık lojistik veya yüksek kurulum maliyetleri, bunların yaygın olarak kullanılmasını engellemektedir.

İleri bir teknoloji olarak ileri osmoz ve basınç geciktirmeli osmoz'dan oluşan osmotik porosesler, atıksuların arıtılması, geri dönüşümü ve yeniden kullanımı ile "Mavi Enerji" olarak adlandırılan tuzluluk gradyan enerjisinin toplanması için öne çıkan teknolojiler olarak düşünülmektedir. Farklı tuzluluk içeriklerine sahip olan çözeltilerin karıştırılmasından çok yüksek miktarda enerj, edilebilmektedir. Bu enerji Tuzluluk Gradyan Enerjisi (TGE) olarak adlandırılmakta olup, uygulanabilir bir yenilenebilir enerji kaynağı olarak görülmektedir. Örneğin, 37300 km^3 yıllık küresel nehir deşarjının denizle buluştuğu yerlerdeki potansiyel olarak elde edilecek gücün, küresel enerji talebinin önemli bir yüzdesini karşılamaya yetecek kadar, neredeyse bir terawat'tan fazla olduğu tahmin edilmektedir.

Tuzluluk gradyanlarının enerji potansiyelinin gerçekleştirilmesi için, mevcut tuzluluk gradyan enerjisinin verimli bir şekilde dönüştürmek için özel tasarlanmış proseslere ihtiyaç vardır. Bu prosesler için basınç geciktirmeli osmoz (BGO), ters elektrodiyaliz, kapasitif karıştırma ve hidrojel şişmesi dahil olmak üzere çeşitli işlemler tasarlanmıştır. Bu proseslerden en yaygın şekilde araştırılan BGO, düşük konsantrasyonlu besleme çözeltisi ile yüksek konsantrasyonlu çekme çzöeltisi arasında yarı geçirgen bir membran kullanılır.

İki çözelti arasındaki kimyasal potansiyel fark sayesinde çözünen maddeler tutulurken, su moleküllerini besleme tarafından çekme çözeltisi tarafına yönlendirir. Çekme çözeltisi bölümündeki hacim genişlemesi daha sonra çekme çözeltisi tankının hidrolik basıncını arttırmak için sınırlandırılır ve sonuçta ortaya çıkan basınçlı su akışı, güç üretmek için bir hidro türbin boyunca gönderilir.

Bununla birlikte ileri osmoz (FO) ve basınç geciktirmeli osmoz (PRO) henüz geliştirilme aşamasındadır. Osmotik güçten elektrik enerjisi üretme fikri yarım asırdan fazla bir süre önce kabul edilmiş olmasına rağmen, BGO pratik uygulamalarda henüz yerini alamamıştır. Bu teknik için en büyük engel BGO sistemi için uygun membranın eksikliğidir. Ancak, BGO için membran malzemeleri geliştirilmeye başladığı için BGO prosesleri son zamanlarda araştırmacıların ilgisini çekmektedir.

Yüksek su geçirgenliği ve mükemmel iyon tutma özelliği sağlayan ozmotik membranlar üretmek kolay değildir. İdeal bir ozmotik membran, yüksek su geçirgenliğine ve düşük ters tuz akış oranına sahip olan koşulları karşılayan ince bir film kompozit membran olabilir. Bununla birlikte, membranın PRO sistemlerde nispeten yüksek hidrolik basınçlara dayanması için bazı mekanik özellikler hayati önem taşır. Neyse ki, elektrospinning yöntemi ile üretilen membranlar, gözenekli yapı özellikleri ve kolay üretimi nedeniyle mükemmel destek katmanının tüm gerekliliklerinin üstesinden gelmek için mükemmel bir yeteneğe sahiptir ve bu nanomalzemeler, nanofiberlerin mekanik mukavemetini arttırmak için entegre edilebilir. Bunun dışında, çok ince bir seçici poliamid kaplama elde etmek için elektrospun nanofiber membrana arayüzey polimerizasyonu (AP) gerçekleştirilebilir. İFK membranları, nano katkı maddelerini destek katmanlarına entegre ettikten sonra osmotik olarak kullanılan membran proseslerinde muazzam potansiyel gösterebilir.

Bu tezin amacı, güçlendirilmiş basınç geciktirmeli ozmoz membranlarının geliştirilmesi üzerine kapsamlı bir çalışma tasarlamak ve yürütmektir. Spesifik olarak, bu tez, BGO prosesleri için mükemmel bir mekanik mukavemet gösterirken, yüksek su geçirgenliği ve solventler için mükemmel seçiciliğe sahip yeni nanofiber destekli ince film kompozit membranların geliştirilmesini sunmaktadır. Arayüzey polimerizasyon reaksiyonları, destek tabaka üzerinde çok ince poliamid seçici tabaka oluşturmak için kullanılmış ve bir dizi destek tabakasını imal etmek için elektrospinning işlemi kullanılmıştır.

Öncelikle, BGO membranları imal etmek için destek katmanı olarak düz plaka elektrospun poliakrilonitril nanolifleri kullanma potansiyelini araştırılmıştır. Poliamid İFK çalışmaları %16 PAN polimer çözeltisinde % 0,1,2,5,10 kristal nanoselüloz (CNC) içeren beş farklı destek tabakasına başarıyla uygulanmıştır. BGO membranlar, özel üretim düz plaka membrane üretim ünitesi ile başarıyla üretilmiştir.

PAN ve CNC'nin SEM, FTIR, DMA ve temas açısı ölçüm analiz bugularına göre tamamiyle karışım sağladığı sonucuna varılmıştır. CNC'nin PAN polimerine eklenmesi sonucunda, BGO uygulamalarında ana problem olan destek katmanlarının mekanik gücünü artırdığı görülmüştür. Yeni geliştirilen membranla , 1 M NaCl çekme çözeltisi ve deiyonize su besleme solüsyonu kullanarak 300 LMH'lik yüksek bir BGO su akısı elde edilebilmiştir. Çalışmanın bu bölümünde ters tuz akısı ise 1.5 gMH olarak bulunmuştur. Su akısının ters tuz akısına oranını temsil eden (J_w/J_s) oranı ise BGO işletimi sırasında 200 L/g olarak bulunmuştur. Düz plaka İFN BGO membranların üretiminden sonra modül paketleme yoğunluğunu artırabilmek için iyileştirmeler yapılmıştır. Bu noktada, BGO uygulamaları için tubuler şeklindeki membranları imal etmek için yeni bir teknik kullanılmıştır.

Yeni üretilen tübüler membran, besleme suyu olarak deiyonize su ve çekme çözeltisi olarak 1M NaCI kullanarak 405.38 LMH'lik daha yüksek bir BGO su akısı elde etmeye imkan sağlamıştır. Bu noktada tübüler membranlarla düz plaka membranlara nazaran daha yüksek ters tuz akısına ulaşılmıştır. Su akısının ters tuz akısına (Jw / Js) oranıyla temsil edilen değer ise bu çalışmada BGO işlemi için 193,03 L/g kadar yüksek tutulabilmiştir. Bildiğimiz kadarıyla, bu tez çalışmasında geliştirilen membranın performansı, daha önce literatürde yayınlanan tüm BGO membranlardan daha iyi performans göstermiştir.

1. INTRODUCTION

To overcome the global energy scarcity and to reduce the dependency of many countries on fossil fuels, the production and utilization of renewable energy sources are needed. Salinity gradient energy (SGE) is tougth to be possible candidate for sustainable energy due to the availability of saline waters mixed with less saline solution around the world. Pressure retarded osmosis (PRO) is one of the most important technologies to generate energy from salinity gradient. Thus far, a comprehensive method have not be found for mitigating pressure retarded osmosis membrane deformation problem. Crystal nanocellulose (CNC) is a very appropriate nanomaterial completely mixed with the polyarylonitrile (PAN) polymer matrix for fabrication a novel strong enough nanofiber based pressure retarded osmosis membrane.

This thesis consist of a comprehensive study on the development of nanofiber based pressure retarded osmosis membranes with crystal nanocellulose (CNC) addition. Purpose of thesis, unique aspect and organization of the thesis are given below.

1.1 Purpose of Thesis

In this thesis, it was aimed that the use of a novel nanomaterial in order to fabricate a flat sheet and tubular reinforced pressure retarded osmosis membrane. CNC nanomaterials are of natural origin and are readily available in large quantities. In addition, it can give higher water flux to membranes produced with CNC hydrophilic structure and make nano fibers stronger. Due to these advantages, the following objectives were planned:

- Determination of the polymer type and the concentration which is support layer membranes will be fabricated,
- Complete dissolving of CNC in the used polymer solution,
- Fabrication and characterization of nanofiber based TFN flat sheet pressure retarded osmosis membranes in a tailor made equipment,

- Evaluation of flat sheet pressure retarded osmosis performance in the process,
- In order to increase the packing density, fabrication of novel tubular membranes and evaluate the performanes.

1.2 Unique Aspect

The novel side of the thesis are fabrication of crystal nanocellulose (CNC) doped polyarcylonitrile (PAN) nanofiber based TFN pressure retarded osmosis in both flat sheet and tubular forms. It is critical understanding the effect of CNC in PAN polymer matrix. The reinforcement of the PAN precursor fiber using CNC offers a unique strategy to improve the mechanical strength of the total PRO membrane. The results of the studies proved that according to the ratios increased from 0 to 10% of CNC, youngs' modulus of the fabricated membranes show up to 675% increase on final membranes. Besides its reinforcement effect water flux and reverse salt flux values were found as 300 LMH and 1.5 gMH in flat sheet membrane and also 405.38 LMH and 2.10 gMH in tubular membrane respectively which is the highest values reported in the literature.

1.3 Organization of the Thesis

The thesis contains an introduction followed by two review articles and two data chapters (Chapters 2-5), and thesis conclusions and recommendations (Chapter 6). Each data chapter comprises of research aims and results.Chapter 2 covers research on the energy applications of nanofiber membranes. In this section, the fabrication of nanofiber membranes, electrospinning methods, precursors used in nanofiber membrane fabrication, characterization methods of nanofibers and their applications in the field of energy (lithium-ion batteries, solar cells, dye-sensitized solar cells, supercapacitors, hydrogen storage and pressure retarded osmosis) are included. In the 3rd chapter, common types of nanocellulose material, extraction processes and application areas of nanocellulose nanocomposites (composite and filling material, paper and packaging industry, electronics industry, biomedical applications and filtration/purification processes) are discussed. Besides that, information is given about process parameters affacting the electrospinning method and the compability of CNC with the electrospinning method. In the 4th chapter, the results of PAN/CNC

nanocomposite flat-sheet nanofiber pressure retarded osmosis membrane fabrication, characterization and testing in the processes are given. In the 5th chapter, the results of PAN/CNC nanocomposite tubular nanofiber pressure retarded osmosis membrane fabrication, characterization and testing in the process are given. In the 6th chapter, there are general evaluation and suggestions about new studies that can be done in the future in the light of the data obtained from the results of the research in all parts of the thesis.

2. LITERATURE REVIEW[1]

2.1 Nanofiber Membranes for Energy Applications

Energy-related issues are one of the most significant challenges of the twenty-first century. Almost 80% of global energy consumption is met from non-renewable, carbon-intensive fossil fuels (Figure 2.1). Extensive use of fossil fuels brings about environmental problems due to extensive reliance and puts severe pressure on the global economy. Since these resources are limited and will be consumed up (not anytime in near future but eventually), converting energy supplies to sustainable sources and developing new technologies for clean energy conversion, storage and conversation are essential (Peng et al, 2016; Dong et al, 2011).

Solar cell and fuel cells are main energy conversion devices whereas supercapacitors, batteries and hydrogen storage devices are energy storage devices. These devices are environmentally friendly and produce little pollution. Nanomaterials have uniqu properties due to their high surface to volume ratios, and these materials can be found as nanoparticles, nanopowders, nanorods, nanotubes and nanowires.

Currently, these nanostructured materials are synthesized by methods such as chemical vapor deposition, wet chemical synthesis, sol-gel, self-assembly, and electrospinning. Other than electrospinning, methods has some limitations in terms of material restrictions, high cost as well as high process complexity (Dong et al, 2011). On the other hand, electrospinning is used to fabricate nanofibers which are extensively used for energy area in terms of developing energy conversion and storage devices due to their high surface area, controllable porosity and ease of accessibility. Electrospinning is an efficient and low-cost method and offers to fabricate different morphologies such as core-shell, hollow, multilayer, porous (Sun et al, 2016). Proper selection of material,

[1] This chapter is based on Mehmet Emin Pasaoglu, Ismail Koyuncu and Reyhan Sengur-Tasdemir. 2019. Chapter 10-Nanofiber Membranes for Energy Applications, In: Nanofiber Membranes for Medical, Environmental and Energy Applications, CRC Press. ISBN: 97880815387039

electrospinning parameters and characterization are particularly important for achieving these morphologies.

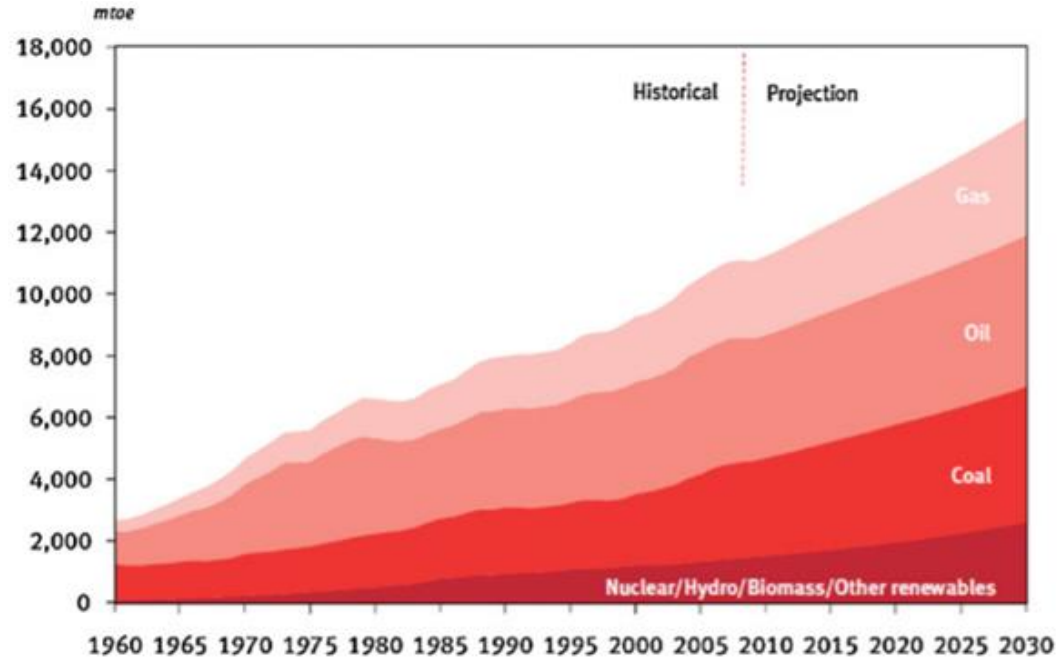


Figure 2.1 : World energy supply according to fuel type (Reprinted from *J.Power Sour*., 196, Dong, Z. et al., Electrospinning materials for energy-related applications and devices, 4886–4904, Copyright 2011, with permission from Elsevier).

In this chapter, first materials used for nanofiber membrane formations are investigated, followed by deep insights into nanofiber membrane fabrication and characterization.

Information related to nanofiber membrane applications for energy- related field are summarized in terms of fuel cells, supercapacitors, solar cells, lithium-ion batteries, hydrogen storage and pressure retarded osmosis (PRO).

2.2 Nanofiber Membrane Fabrication

Various engineering fields involved in nanoscale materials such as nanofibers in the fibre industry. Nanofibers are defined as fibres with a diameter of 100 nm or less, Ramakrishna (2005) and remarkable for their characteristic features such as larger surface area to volume ratio, extremely small pore diameters and superior mechanical properties (Huang et al, 2003). Due to these chacteristic features, nanofibers have very wide range of application fields such as filtration, battery separator, wound dressing, vascular grafts, enzyme immobilization, electrochemical sensing, composite materials,

reinforcements, blood vessel engineering and tissue engineering (Bergshoef and Vancso, 1999; Bhattarai et al, 2004; Xu et al, 2004; Nayak et al, 2011).

Because of the process limitations, existing fiber technologies cannot produce strong fibers with diameter smaller than 2 μm. The most commonly used process for nanofiber fabrication is electrospinning (Patanaik et al, 2007; Zhou and Gong, 2008). The reason of using electrospinning is due to its simplicity and suitability for allowance to use different polymers, ceramics and metals. There are other methods in the literature including melt blowing, flash spinning, bicomponent spinning, phase-separation and drawing. Nanofiber mats known as nanowebs are using for collecting fibers having several nanometers to hundreds of nanometers scale (Nayak et al, 2011).

2.2.1 Electrospinning

Electrospinning is a technique originated back to Formhals patent for the production of artificial filaments using high electric field in 1934. This technique was mainly based on the effect of electrostatic charged liquid material which forms a cone shape near a droplet , if the charge density is very high small jets may be ejected from the tip of the cone (Formhals, 1934). Electrospinning process mainly classified as solution electrospinning and melt electrospinning. Polymer properties affect type of electrospinning process.

Many researches have been reviewed the factors affecting characteristic features and different applications of the nanofiber web (Bognitzki et al, 2001; Duan et al, 2004; Koski et al, 2004; Mckee et al, 2004; Lin et al, 2004). Solution electrospinning method includes the use of toxic solvents. Therefore, additional solvent extraction step is needed. Because of this reason, solution electrospinning process has some drawbacks such as low productivity (up to 300 mg/hr) and environmental concerns.

On the other hand, melt electrospinning has higher viscosity of molten polymer. The biggest challenge about application of polymeric melt is electrical discharge problem. This problem leads difficulties inherent in finer fiber formation.

In order to obtain higher productivity in solution electrospinning variable number of jets adopting different techniques such as: (a) multi-jets from single needle, (b) multi-jets from multiple needles and (c) needless systems.

(a) Multi-jets from single needle: Single needle electrospinning (SNE) defines as a single-jet initiated from the Taylor cone by applying an electric field. Yamashita et al. (2007) introduced the use of multi-jets for the first time. Polybutadiene (PB) beadless membranes were prepared by growing multi-jets at the needle tip of an SNE setup. Significant discrepancy in electric field distribution and degree of solution blockage at the needle tip were suggested as two possible formation mechanisms for the formation of multi-jets in an SNE. Vaseashta (2007) used another approach for the formation of multi-jets from multiple Taylor cones in an SNE system using a curved collector. Multi-jets can be applied from a single needle using separate polymer sub-jets on its path to the collector.

(b) Multiple-jets from multiple needles: Multiple needle electrospinning (MNE) systems are less studied in literature (Regele et al, 2002; Kim et al, 2006; Lee et al, 2006; Teo et al, 2007). Needle configuration, numbers and dimensions are determining factors for MNE systems. Needle configurations for MNE systems are linear configuration and two-dimensional configurations (Figure 2.2). Linear and two-dimensional configurations have sub-divisions such as elliptical, circular, triangular, square and hexagonal. While using MNE systems setup, large operating space and more carefully design between needles in order to beware of strong charge repulsion between the jets (Nayak et al, 2011).

(c) Multi-jets from needleless system: One of the most popular systems is needleless electrospinning, which is substantially improved by provoking numerous polymeric jets from free liquid surfaces. Principle of a needleless electrospinning system is as follows: when the applied electric field reaches above a critical point, electrically conductive liquid start to form jets. Yarin and Zussman (2004) was first reported needless electrospinning. At this work, two layered system combination was used. Lower layer consists of a ferromagnetic suspension and the upper layer was a polyethylene oxide (PEO) solution. With this method numerous continues spikes can be generated using magnetic field at the available surface of the magnetic-fluid. Application of high voltage to polymer layer creates visible perturbations at the surface of the polymer layer. Electrode collected fibers from multiple jets after it reached a critical voltage (Nayak et al. 2011).

Jirsak et al. (2005) studied the formation of multi-jets from the free surface of a liquid uploaded in a slowly rotating horizontal cylinder. Elmarco Company (Liberec)

commercialized this method under the brand name of Nanospider™. Dosunmu et al. (2006) presented a novel needless electrospinning method which includes a cylindrical porous polyethylene (PE) tube for the fabrication of nanofibers from multiple jets of nylon 6,6 solution.

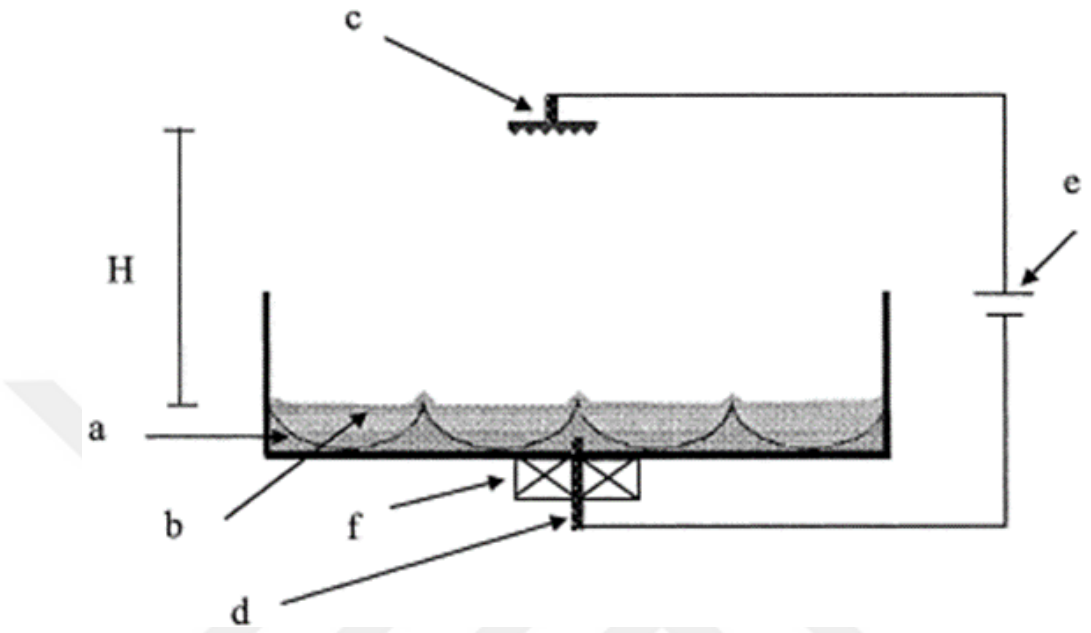


Figure 2.2 : Schematic drawing of the experimental setup. (a) Layer of magnetic liquid, (b) layer of polymer solution, (c) counter-electrode located at a distance H from the free surface of the polymer, (d) electrode submerged into magnetic fluid, (e) high voltage source, and (f) strong permanent magnet or electromagnet. (Reprinted from *Polymer*, 45, Yarin, A. and Zussman, E., Upward needleless electrospinning of multiple nanofibers, 2977–2980, Copyright 2004, with permission from Elsevier).

In this method, electricity applied from the bottom of the tube. pressurized air goes through the walls of the porous tube until it reaches top of the tube. Fiber diameter was similar single jet electrospinning with a broader distribution range.

Another needleless electrospinning system has been reported by Wang et al. (2009). In the study, a conical metal wire coil was used as the spinneret and polyvinyl alcohol (PVA) nanofibers were fabricated. The advantage of needleless system is the possibility of producing finer nanofibers on a larger scale compared to conventional electrospinning.

(d) Other potential approaches in electrospinning: Alternative to needle including and needleless systems mentioned above, electrospinning may also be classified into a confined feed system (CFS) and unconfined feed system (UFS). In CFS system, the

polymer solution or melt is injected by a syringe pump at a constant rate. The advantages of CFS are:

• Controlled flow rate
• Uniform fiber diameter
• Better fiber quality

Besides CFS has some disadvantages such as increased system complexity and prone to clogging. In UFS, the polymer solution or melt flows unconstrained over the surface of another material. UFS includes bubble electrospinning; electro blowing; electrospinning by using a porous hollow tube, a micro fluidic manifold and roller electrospinning (Nayak et al, 2011).

(a) Bubble electrospinning: Bubble electrospinning is explored by, Liu and He (2007) for the mass production of nanofibers. System components are a high-voltage DC generator, a gas pump and a vertical liquid reservoir where opening in lid exist, a gas tube is centered at the bottom of the reservoir, a thin metal electrode and a grounded collector.

(b) Electro blowing: Electro blowing is an electrospinning process which is conducted with air blowing. Under high voltage, polymer solution which dissolved in a solvent is pumped through a nozzle (Figure 2.3) Compressed air is injected through the lower end of the spinning nozzle and fibers

are collected on a grounded collector. In electro blowing, simultaneously electrical force and air blowing shear force interact with each other to fabricate the nanofibers from the polymeric solution. Electro blowing nanofiber process is suitable both thermoplastic and thermosetting resins (Nayak et al, 2011).

2.3 Nanofiber Membrane Precursors Used for Electrospinning

Electrospinning is possible if molecular weight of the polymer is high enough. Therefore it can be applicable to almost all soluble polymer. As explained before, many operation parameters such as polymer molecular weight, applied voltage, solution feed rate and spinning distance; environmental parameters such as temperature, humidity, air velocity and solution properties such as conductivity, viscosity and surface tension affects nanofiber morphologies.

Natural polymers, polymer blends, ceramic and metal/metal oxides can be used as precursors to tune beaded, ribbon, porous, core-shell and aligned nanofiber morphologies (Dong et al, 2011).

The most widely used precursor in electrospinning is polyacrylonitrile (PAN). PAN is an environmentally friendly material, commercially available.

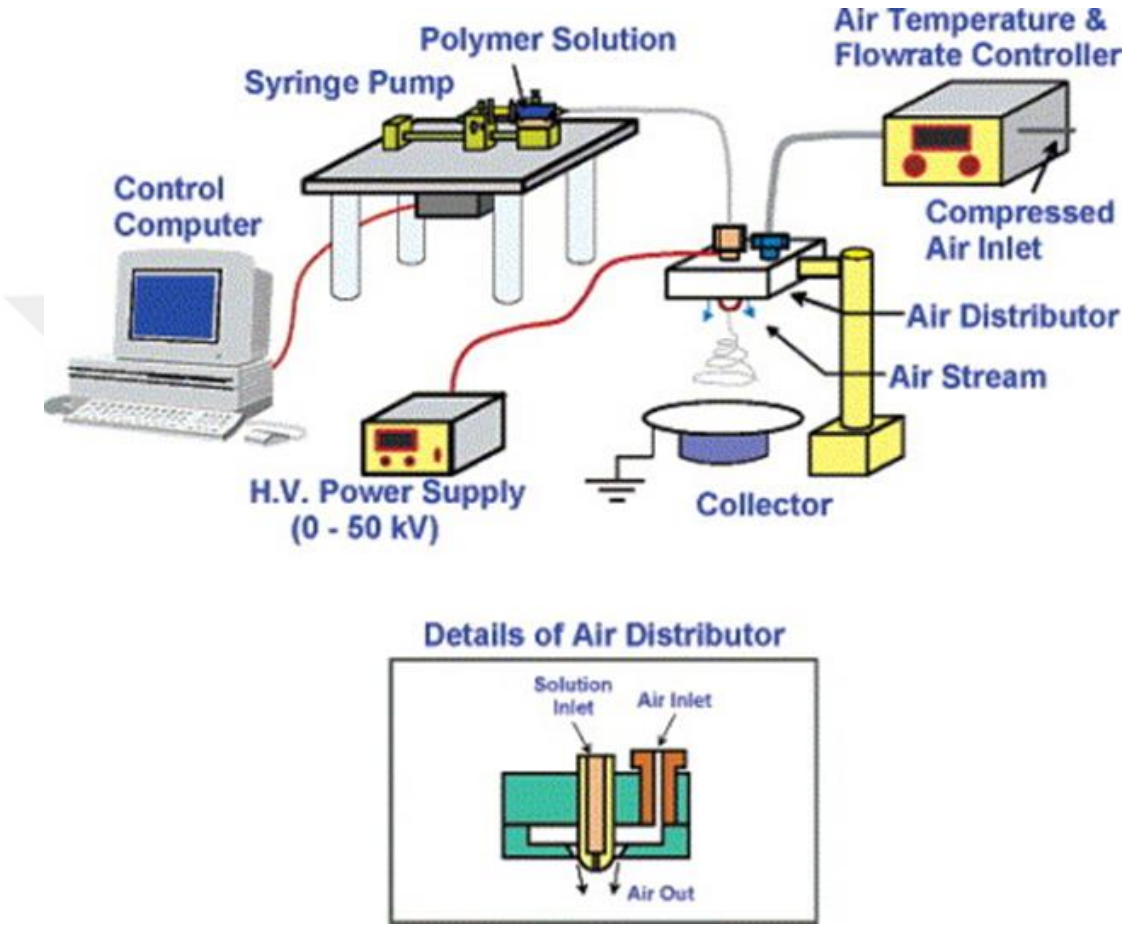


Figure 2.3 : Electroblowing setup. (Reprinted from Polymer, 46, Wang, X. et al., Formation of water-resistant hyaluronic acid nanofibers by blowing-assisted electro-spinning and non-toxic post treatments, 4853–4867, Copyright 2005, with permission from Elsevier).

It has more than 50% carbon yield, excellent mechanical properties and uniform carbon fibers can be easily obtained.

Almost 90% of all nanofibers today are produced with PAN (Peng et al, 2016; Zhang et al, 2016). Another highly preferred precursor is pitch which has high carbon yield with low cost. Tetrohydrofuran (THF) is known as appropriate solvent for pitch. High solution viscosity is needed for the spinning of pitch. In general, PAN is added into pitch where the increase of spin ability and a decrease are needed in the diameter of

fibers (Zhang et al, 2016). Natural polymers that can be used for the fabrication of nanofiber for energy applications are lignin and cellulose. Lignin has a great potential for fabricating electrospun nanofibers. Lignin-based nanofibers have large specific surface area whereas low carbon yield is obtained (around 20%–40%). Examples of cellulosic material can be found for the reinforcement of lithium ion batteries (Chiappone, 2016).

Moreover, as membrane materials, examples of the use of polycarbosilane, Rose et al. (2010), poly(vinylidenefluoride) (PVDF), Yang et al. (2011), cellulose Deng et al. (2013), phenolic resin Bai et al. (2014), poly(vinyl alcohol) (PVA), Fatema et al. (2011), polyimide (PI), Yan et al. (2014), polyvinylpyrrolidone (PVP), Wang et al. (2012), Poly(methylmethacrylate) (PMMA) and polystyrene (PS) can be found in literature (Peng et al, 2016). PI has an electrical conductivity when carbonized and it has a similar carbon yield to PAN.

PVA has a low carbon yield (around 3%–10%); however, its carbon yield can be increased to 40%–50% by using an appropriate treatment. Although PVP has a low carbon yield, it is attractive due to its solubility in different solvents. Both PVA and PVP material can form hybrid complexes with metal oxides. PVDF has excellent mechanical properties where they can be substitutes for propylene-based Celgard separators. To increase its ionic conductivity, PVDF can be modified with PEO or SiO_2 nanoparticles. PMMA and PS are used as sacrificial polymers where they can create void spaces (Thavasi et al, 2008; Zhang et al, 2016). Carbide derived polycarbosilane material has a potential to be used in supercapacitors and hydrogen storage due to its high surface area, narrow and tunable pore size distribution, etc. Phenolic resins can be novolac type or resole type and is used as alternatives for overcoming drawbacks of PAN. Bai et al. (2014) showed that adding electrolyte to spinning solution can enhance the conductivity and electrostatic repulsion where the diameters of produced phenolic fibers were reduced. In the literature, also Pt (Kim et al, 2009a, 2010; Shu and Li, 2009), TiO_2 (Song et al, 2005; Onozuka et al, 2006; Shim et al, 2009; Chandrasekar et al, 2009), CNT (Hu et al, 2007; Lu et al, 2009), Si (Ji et al, 2009; Ji and Zhang, 2009), Sn (Yu et al, 2009; Zou et al, 2010), PEO (75), Nafion (Choi et al, 2008), PVDF-HFP (Park et al, 2008; Kim et al, 2009b), LiCoO2 (Gu et al, 2007), Fe_3O_4 (Wang et al, 2008), Cu (Ji et al, 2010), Mn_3O_4 (Fan and Whittingham, 2007), CO_3O_4 (Gu et al, 2008; Ding et al, 2008), piezoelectric materials such as PZT

(Xu et al, 2006; Hossain and Kim, 2009), V-ZnO (Chen et al, 2009, 2010) and thermoelectric materials such $NaCO_2O_4$, $Ca_3CO_4O_9$ (Maensiri and Nuansing, 2006; Yin et al, 2010) were used for electrospinning.

2.4 Nanofiber Characterization

For the characterization of nanofibers; fiber diameter, diameter distribution, fiber orientation and morphology, pore size, mean pore size etc; molecular structure, super molecular structure, surface chemical properties; transport properties such as electrical, thermal, and mechanical properties should be determined (Huang et al, 2003).

Fiber properties can be determined by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). TEM has an advantage over SEM since it allows observation of polymer solution and it does not require a dry state of sample. Mean pore size, maximum pore size and pore size distribution can be determined by porometer. To determine molecular, super molecular structures and surface chemical properties, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), optical birefringence, wide-angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXC), differential scanning calorimeter (DSC), Raman spectroscopy, XPS, water contact angle can be used (Huang et al, 2003; Wang et al, 2003). Mechanical properties of a single nanofiber is challenging due to its very small dimensions. However in the literature, studies showed that data related to tensile strength, young's modulus etc. were obtained by material testing systems (Zhang et al, 2015). Electrochemical properties can be determined by impedance spectroscopy, cyclic voltammetry (Zhuang et al, 2018). Also for nanofibers, surface area is important and it can be determined by Brunauer–Emmett–Teller (BET) method (Zhuang et al, 2018).

2.5 Nanofiber Applications in Energy Field

2.5.1 Lithium- ion batteries

Conventional energy storage technologies (Ni-Cd and Ni-Mh batteries) have 2–3 times lower energy and 5–6 times lower power densities compared to lithium-ion batteries.

Therefore they offer an effective solution and advantages in terms of high coulombic efficiency, low self-discharge, high operating voltage, and no "memory effect." Working principle of Li-ion batteries is transferring of Li ions where exist in an electrolyte solution between two electrodes (cathode and anode). Between electrodes, there is a separator membrane which prevents physical contacting of electrodes. Schematic of Li-ion battery is given in Figure 2.4. At the charged state of the battery, an external power source injects electrons into anode. Some Li ions are given up from cathode and move to the anode through electrolyte at the same time.

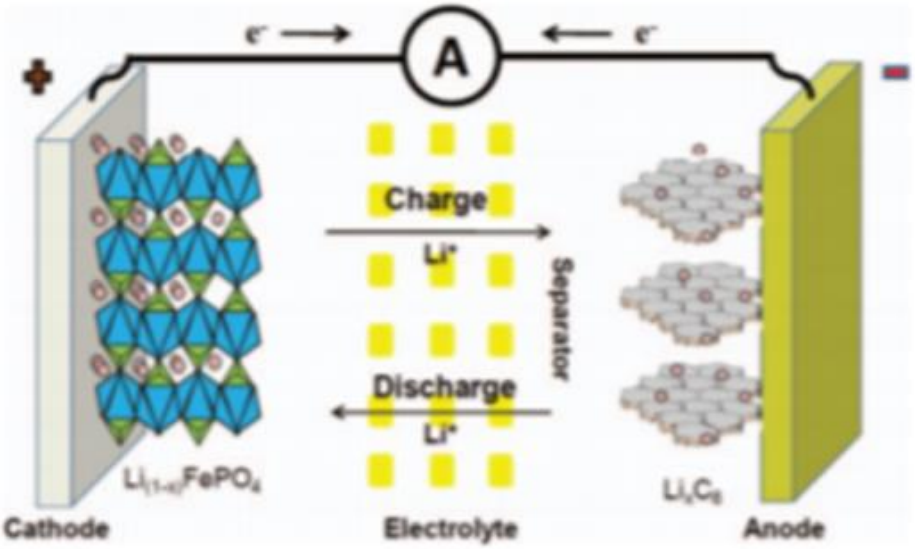


Figure 2.4 : Schematic of Li-ion batteries (Reprinted from Polym. Rev., 51, Zhang, X. et al., Electrospun nanofiber-based anodes, cathodes, and separators for advanced lithium-ion batteries, 239–264, Copyright 2011, with permission from Elsevier).

During the process, chemical energy is stored in the battery as electricity. When battery starts to discharge, Li ions return back to the cathode through electrolyte, and electrons are released to the outer circuit for doing electrical work. In existing Li-ion batteries, active powder materials (graphite powder for anode and $LiFePO_4$ for cathode) are used to store energy; however, they have disadvantages of having long diffusion path for lithium ions and slow electrode kinetics which prevent revealing of their true performance. In addition to this, as separator membranes conventionally microporous polyolefin materials are used. Although these membranes have good chemical and reasonable mechanical strength, they suffer from low thermal stability, low porosity and poor wettability with polar liquid electrolyte that result in high cell resistance,

reduced energy density, and low rate capability of rechargeable lithiumion batteries (Qiao and Wei, 2012).

At this point, electrospun fibers gained attention as electrodes due to having shorter diffusion paths compared to powder materials; also there are relatively large number of lithium insertion sites, which decrease the charge transfer resistance at the interface between electrolyte and active electrode material and their high area/mass ratio, which enable faster intercalation kinetics. Besides they are good candidates as electrodes, electrospun nanofibers are also good candidates as separator membranes due to their small pore size, high porosity and enabling high rate charge/discharge of batteries (Zhang et al, 2011).

Sony has fabricated first Li-ion battery. In this battery, they have used a layered oxide such as lithium cobalt oxide as cathode material. This material has advantage of having high specific energy density, low self-discharge and excellent cycle life whereas solid state diffusion phenomena make it disadvantageous. In addition to lithium cobalt oxide, scientists have used manganese spinel based, lithium iron phosphate and other phosphoolivine materials. However, studies showed that electrospun nanofibers are preferable because they offer shorter diffusion distance of Li+ ions. Studies also showed that making core-shell nanostructures increased the cycle ability of batteries. As mentioned before, $LiFePO_4$ material performance can be increased by carbon coating and producing $LiFePO_4$/amorphous carbon composite layer (Dong et al, 2011).

The most popular material used as anode is carbon due to its low and flat working potential, long cycle life and low cost. Yet carbon material has low charge capacity and to solve this problem non-carbon materials are incorporated to increase charge capacity (Zhang et al, 2011). For this purpose, Si is used which increase the capacity of Li insertion and de-insertion during cycling. One drawback of using Si is the mechanical failure resulted from large volume changes during insertion/de-insertion.

Alternatively Ni, Co and Sn, MnO_x and Fe_3O_4 have used in the literature to increase the capacity of carbon systems.

Currently, in many of commercial Li-ion batteries as separator, microporous polymer membranes are used. These membranes exhibit good chemical stability, suitable thickness, and reasonable mechanical strength. On the other hand, these membranes have low thermal stability, low porosity and poor wettability which resulted in

decreased battery performance. Perovskite-type lithium lanthanum titanate, which is an ionic conducting ceramic particle used in electrospun nanofiber can be an option to enhance battery kinetics in terms of good cycle ability, high rate capability due to having large liquid electrolyte uptake, high ionic conductivity, good electrochemical stability and reduced electrode-electrolyte interface resistance (Zhang et al, 2011). Cellulose fibers are used as separators for reinforcing polymeric membranes in Li-ion batteries. Cellulose has capability to improve movements of polymer chains to achieve higher ion mobility and enhance mechanical strength. This can be resulted in the use of thin composite electrolytes for flexible devices and enhance safety by introducing more robust separators. Mostly cellulose applications include the reinforcement of PEO material (Azizi Samir et al, 2004a, 2004b, 2005; Chiappone et al, 2004; Alloin et al, 2010; Gerbaldi et al, 2011). There are some examples of the use of chitin in PEO and PVDF-HFP material (Angulakshmi et al, 2010, 2011 2013; Stephan et al, 2009) for the same purpose as cellulose. In these examples, it is stated that chitin increased the mechanical properties as well as ionic conductivity and transference number of the electrolyte.

2.5.2 Solar cells

Crystalline silicon solar cells were developed by Chapin et al. (1954) having 4.5% conversion efficiency. Since this development, energy technology has gone through three stages: monocrystalline and polycrystalline silicon, amorphous silicon thin film, and the third-generation solar cells such as dye-sensitized solar cells and hybrid solar cells bringing a new concept. Electrospun nanofiber materials are one of the most efficient strategy introducing of new structured materials (Shi et al, 2015).

2.5.3 Dye-sensitized solar cells

(a) Photoanode: Dye-sensitized solar cells (DSSCs) have the ability to convert light into electricity with the help of a photosensitizing dye. A typical DSSC compound consists of a photoanode, a counter electrode and an electrolyte. Photons absorbed by photosensitizer, then from the photosensitizer, photoelectrons move into the collecting band of semiconductor and photoelectrons are collected on the photoanode. Photoelectrons transfer to counter electrode through the external circuit form current. Maximum light absorption and efficient charge transport affect the total photoelectric conversion efficiency (Shi et al, 2015). At this point, photoanode plays a major role.

Due to their high specific surface area and 1D fibrous morphology thin film coated metal oxide nanofibers with photoanode draw attention (Chuangchote et al, 2008; Cavaliere et al, 2011).

Another commonly used photoanode type is TiO_2 anatase NFs prepared by electrospinning. Because of their poor adhesion to conductive substrate, many techniques have been developed to solve the problem, such as converting electrospun nanofibers into nanorods with the help of hot press pretreatment and ultrathin surface treatment (Song et al, 2004; Fujihara et al, 2007).

(b) Counter Electrodes: Transmitting and collecting electrons made by counter electrode (CE) in DSSCs. The catalytic activity of CE affects the device's internal series resistance changing the fill factor of the counter electrode (Jeong et al, 2014). Because of its high electrocatalytic activities and high photovoltaic performances, Pt counter electrodes are used in DSSCs. But, Pt is expensive and long-term stability is unsatisfactory. Researches continue to develop alternative counter electrodes materials such as carbonaceous materials that can be integrated into transition metal compounds to replace Pt (Shi et al, 2015).

2.5.4 Supercapacitors

Supercapacitors are one of the most promising storage devices in many areas such as transportation, electricity, communication, defense, consumer electronics, and other applications because of their high performance, long cycle life and low maintenance cost. Supercapacitors are classified as pseudo capacitors (PCs) and electrical double layer capacitors (EDLCs). Energy storage is based on fast reversible redox reactions in PCs. Ion adsorption and desorption having role in storing energy in EDLCs. Electrospinning is a method to prepare the highly porous nanofibers. Polymer precursors such as polybenzimidazole (PBI), PAN, and PI are investigated for electrospun carbon nanofibers (CNF). CNF electrospun can be utilized as an electrode for EDLCs after stabilization, carbonization and activation improving surface area and porosity (Shi et al., 2015).

2.5.5 Hydrogen storage

Hydrogen is an important fuel to be used in zero carbon emission vehicles. Hydrogen is three times larger chemical energy density than other chemical fuels. Compared to

gasoline at room temperature, hydrogen volume is 3000 times higher. Therefore it is important find an effective way to store hydrogen in a containment which is compact, light, safe and affordable (Jo, 2012). Hydrogen can be stored in the form of metal hydrides and can be adsorbed into the spaces and/or interstices between the atoms in the metal. Potential materials for hydrogen storage are active carbon, carbon nanotubes, graphite powder, active carbon fiber, TiO_2 and $LiTi_2O_4$ nanofibers, etc. (Bavykin et al, 2005; Kim et al, 2005; Park et al, 2005; Chung et al, 2005; Hong et al, 2007). Material porosity is the most important parameter for hydrogen storage, since hydrogen storage is dominated by small pores. Surface area and pore volume are another two parameters that affect hydrogen uptake rate proportionally. Nanofiber membranes are attractive due to their tunable pore size by optimizing the spinning parameters. High-performance nanofiber membranes can also be developed for storing hydrogen in materials that are well structured, highly ordered and having high aspect ratio at nanoscale dimensions (Thavasi et al, 2008; Jo, 2012). Future works should include development of new solid absorbent materials with a high ultra micro pore volume, high surface area and appropriate hydrogen adsorption potential energy for reversible physisorption.

2.5.6 Pressure-retarded osmosis

Energy demand is increasing worldwide and this energy need being met by fossil fuel-based technologies. Fossil-based energy sources has led to increased attention of alternatively energy technologies such as solar, wind, biomass, hydropower, tidal power, ocean thermal energy conversion, etc. (Bui and McCutcheon, 2014).

Salinity gradient energy naturally occurs when freshwater encounter saline water all over the world. Osmosis process can be used for capturing the energy of mixing fresh and saline waters, which is ultimately lost when freshwater dilutes saline water. Estimated of all salinity gradients in the world is 1,4-2,6 TW from which approximately 980 GW (Ramon et al, 2011; Logan and Elimelech, 2012) can be effectively harnessed with an appropriate designed system (Bui and McCutcheon, 2014). An osmotic pressure difference occurs between two solutions from a dilute solution across a semipermeable membrane to a more concentrated draw solution. Hydrostatic pressure applied by the draw side, which is less than osmotic pressure, the osmotic flow is retarded. The Norwegian power company Statkraft estimates that

osmotic power generation may be developed to be competitive with other energy sources without the drawbacks (Bui and McCutcheon, 2014).

Figure 2.5 describes osmotic processes probabilities between fresh and salty water separated by a semipermeable membrane (Cath et al, 2006). Power generation with PRO process could be well explained via PRO osmosis phenomenon at Figure 2.6 shows a schematic diagram of a typical PRO osmotic power process at steady-state flow (Thorsen and Holt, 2003, 2009; Skilhagen et al, 2008). In order to remove impurities, feed streams have to be pretreated to reduce membrane fouling (Han et al, 2015).

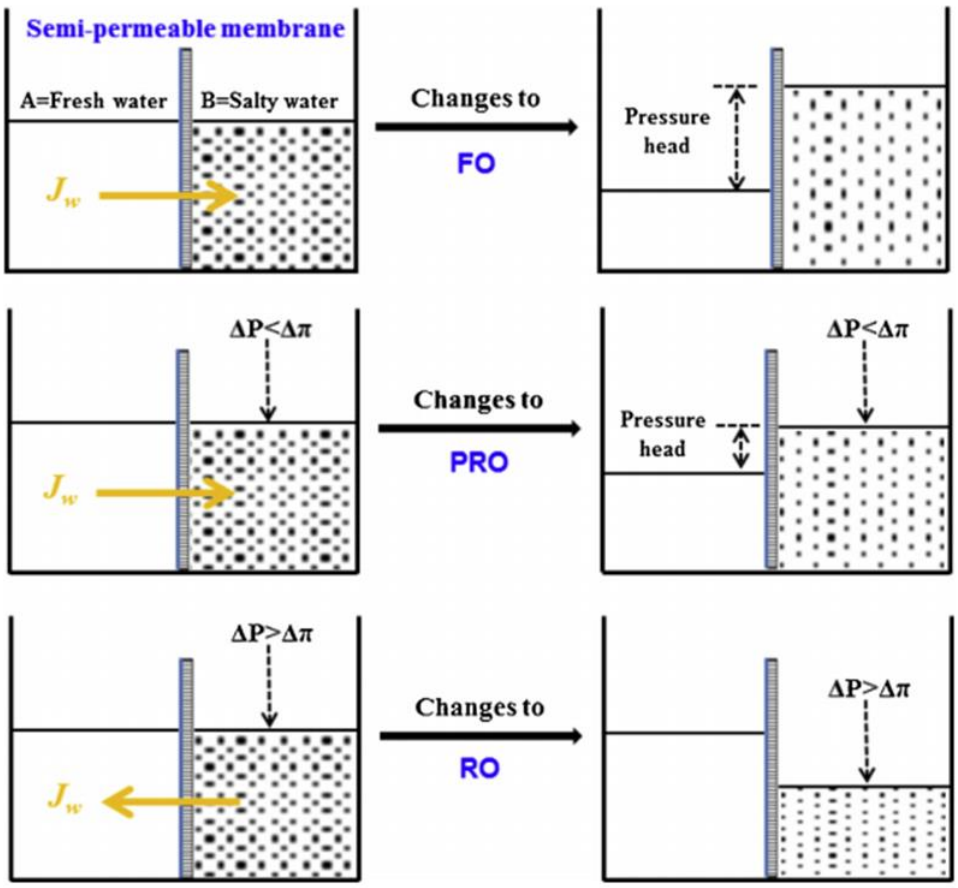


Figure 2.5 : Schematic representation of osmotic processes. Reprinted with permission from (Han et al, 2015).

A novel membrane preparation method found by Bui et al, (2011), flat-sheet polyamide (PA) composite membranes supported by a nonwoven web of electrospun nanofibers. Because of nanofiber's superior porosity, effective area of PA-layer increases. In the study, PSf and polyethersulfone (PES) electrospun nanofiber supports were coated by inter polymerization technique. PA layer shows stronger adhesion to

PSf support rather than PES supports and fabricated membranes displayed five times higher water flux than a commercial osmotic membrane. Electrospinning method is a great promise for forward osmosis and PRO applications (Bui et al, 2011; Alsvik and Hägg, 2013).

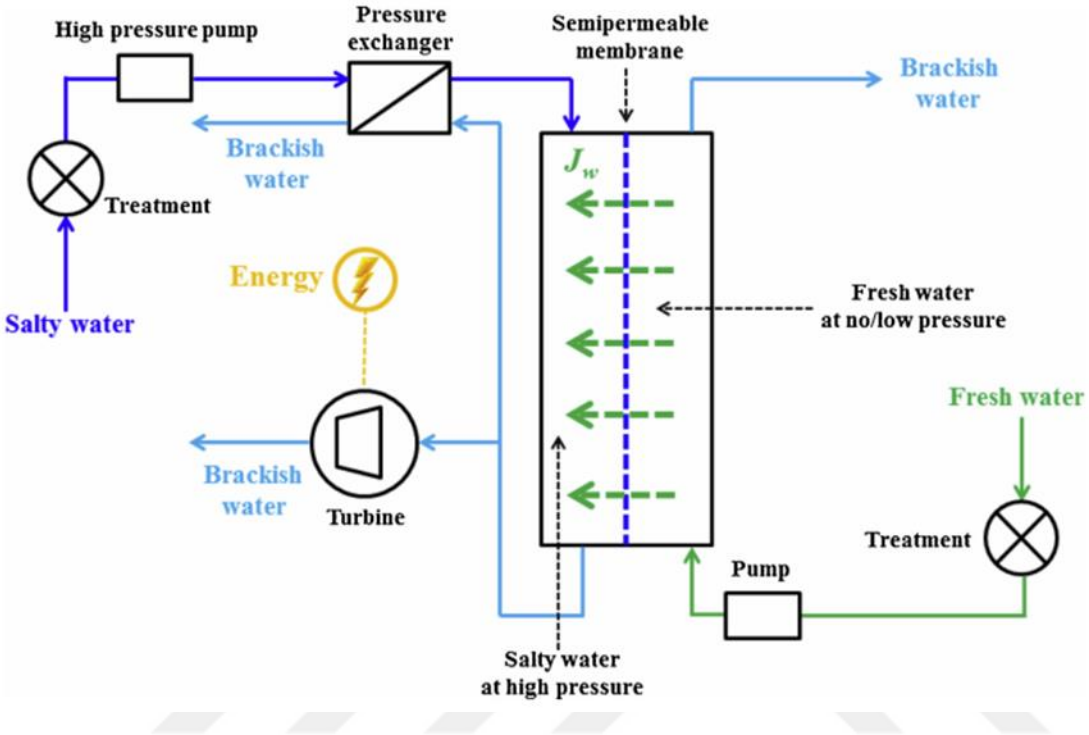


Figure 2.6 : Schematic diagram of a typical PRO osmotic power plant with continuous and steady state flow. Reprinted with permission from (Han et al, 2015).

2.6 Conclusions

Energy is one of the most important concerns for the sake of society in twenty first century. Finding alternative devices to be used in energy applications is getting important. Electrospinning and electrospun nanofibers offers great advantages due to their high surface area, porosity and it is a clean energy alternative. Current advances in electrospun nanofibers deal with conversion and storage of energy. These advances in electrospun nanofibers enable the production of high value added products. Many different materials and different types of electrospinning can be used for the fabrication of nanofibers. Energy-related applications of nanofibers are lithium ion batteries, supercapacitors, hydrogen storage, solar cells, dye synthesized solar cells and pressure-retarded osmosis. For Li-ion batteries due to electrospun nanofiber's high surface area and porosity, high power capabilities and good kinetic properties can be obtained. In the case of fuel cells, nanofibers can be used both as electrolyte

membranes and electrode materials for obtaining high activities and good durabilities. Regarding dye-sensitized solar cells unique fiber morphologies offer high photoelectric conversion efficiencies. High surface area of nanofibers is also effective on electrochemical performance of supercapacitors. Pressure-retarded osmosis nanofiber membranes are used for energy production and it is a new subject needs to be studied.

3. SUBSTITUTION OF PETROLEUM-BASED POLYMERIC MATERIALS USED IN THE ELECTROSPINNING PROCESS WITH NANOCELLULOSE: A REVIEW AND FUTURE OUTLOOK[3]

3.1 Introduction

The increasing need for water in industrial and agricultural areas confronts humanity with water scarcity. Latest studies also shown that 1,3 billion people also insufficient accessibility to clean and secure potable water, while nearly 2,6 billion people have little to no sanitation and millions suffer from water-related diseases annually. Therefore, new technologies and innovations are needed to ensure desalination, water and wastewater treatment. The fusion of nanotechnology with nanotechnology materials provides tremendous potential for improving wastewater and desalination technologies (Ramakrishna and Shirazi, 2015).

Nowadays, in the modern society polymers became essential materials. Over the past 60 years, different technologies improved such as agricultural and food, introduction of functional medical devices, equipment which make the vehicles lighter in order to reduced the fuel consumption by the help polymers. One of the most significant properties of synthesized polymers are high mechanical performance and biodegradability. Due to the easy accessibility of oil and natural gas, they are primarily polymers produced by fuel / fossil derivatives.

- However, the two main factors control the gradual replacement of bio-based polymers with fossil-derived polymers: Increase in oil and natural gas prices leading to higher cost for polymers because of the scarcity of feedstock, and
- The lack of impact on the climate.

Since the Second World War until several years after, world's economy powered by the petroleum-based plastics industry. Today the global economy is being threatened with increasing demand for oil-based raw materials. Petroleum-based raw materials

[3] This chapter is based on "Mehmet Emin Pasaoglu & Ismail Koyuncu. 2020. "Substitution of Petroleum-Based Polymeric Materials Used in the Electrospinning Process with Nanocellullose: A Review and Future Outlook". Chemosphere. DOI: 10.1016/j.chemopshere.2020.128710

have been responsable for the world's climate change. By incineration or other decay process, carbon release from petroleum-derived polymers increases the volume of net greenhouse gas in the atmosphere (Hottle et al, 2013; Iwata, 2015).

It is therefore necessary to remember that scarce resources are carbon raw materials and the years to come would be diminished.

New technologies and manufacturing methods need to be established to reduce the environmental effects produced by the existing polymer industry. The sources of polymers and their properties used in electrospinning / electrospray is shown in Figure 3.1.

Reducing the use of plastics based on petroleum is one of the most sustainable way. The petroleum-based polymers will be substituted in the short term with bio-based polymers (Hottle et al, 2013; Iwata, 2015).

Bio-based polymers are biomass-based materials, according to the European Committee for Standardization (CEN) (European Commission, 2020). This means that bio-based polymers are made primarily of non-fossil materials European Committee for Standardization (2010) and provide a green alternative to conventional polymers based on petroleum. Bio-based raw materials can be found in a number of biological sources, such as agricultural products (corn, potatoes or soybeans), micro-organisms, bacteria, or shellfish (Hottle et al, 2013). They can also be made partly of renewable and synthesized polymers. Examples of commercial bio-based polymers include: Polylactides (PLA) (derived from corn sugar) Halley et al. (2011);Dubey et al. (2017), Polyhydroxyalkanoates (PHAs/PHBs): An intercellular sugar or lipid extracted from a plant is fermented by micro-organisms, producing linear polyesters Halley et al. (2011); Volova et al. (2014), Polyols: sugar-alcohols-derived polymers Halley et al. (2011); Lv et al. (2016), Polyamides: Nylon-11 (poly (undecanoic amino acid)) is a polymer derived from castor oil Halley et al. (2011); Dhanalakshmi et al. (2015), Bio-PET: the bio-poly (ethylene terephthalate) is a combination of bio-based ethylene and other petroleum-based feedstocks Halley et al. (2011), Poulat (2013), Butyl rubber: A green type of organic butyl rubber that is an isobutylene and BioIsoprene^{TM} copolymer Halley et al. (2011); Whited et al. (2010), cellulose acetate: obtained from cellulose present in crops and leaves of plants (Swatloski et al, 2002). Natural polymers are macromolecules and can be constituted in nature which involve proteins (e.g.,

collagen, gelatin, hyaluronic acid, zen, silk), polysaccharides (e.g., sugar, cellulose, alginate, chitosan), terpenes (e.g., natural rubber) and lipids (Sell et al, 2010; Rogina, 2014; Ramakrishna et al, 2006).

In this point, cellulose is a good option to reduce petroleum-based polymer consumption.

The aim of this paper is to show effective use of nanocellulose in electrospinning process while comparing other studies done in the literature and therewithal replacing nanocellulose with petroleum based polymers.

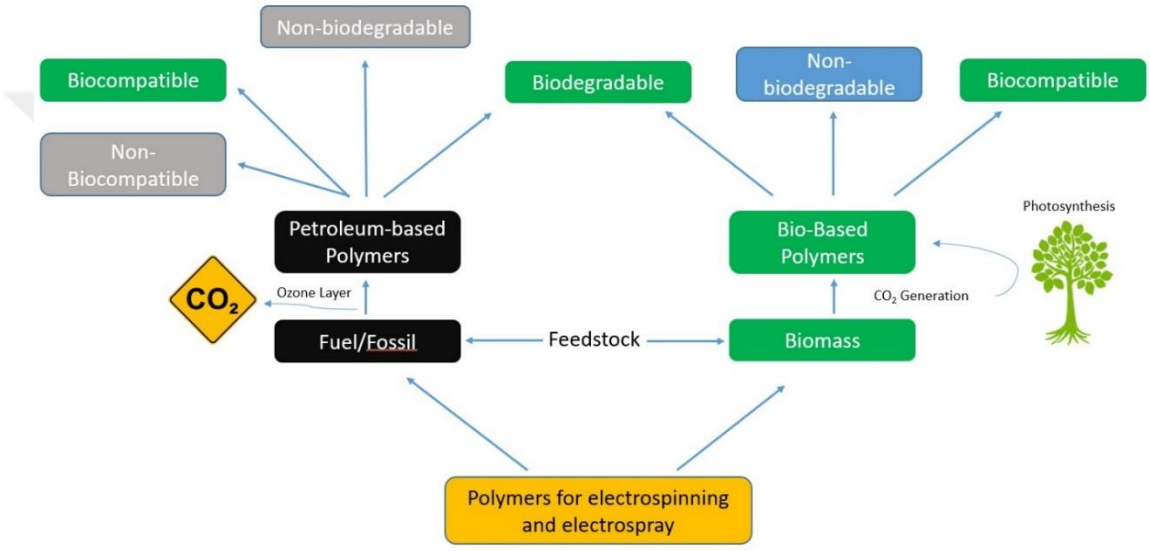


Figure 3.1 : Sources and properties of polymers used for electrospinning / electrospray (Redrawn with permission, from (Soares et al, 2018).

3.2 Nanocellulose

Cellulose naturally exist in the plant cells of wood and cotton. This is the most abundant substance in nature and the primary part of the cell wall of trees and plants. Cotton has the largest cellulose content in plants with about 90% cellulose relative to wood around 40–50% cellulose or bast fabrics, for instance flax, hemp or ramie, with a cellulose content of around 70–80% (Han and Rowell, 1996; Varshney and Naithani, 2011). In contrast with wood and trees, cellulose can also be present in various forms of bacteria, coral, and urochordata, a marine mammal made up of proteins and carbohydrates.

Cellulose cells are a linear homo-polysaccharide composed of D-anhydroglucopyranosis units (AGUs) connected in the same manner as β-1,4-glycosidic bonds. Each other AGU rotates 180° with its counterpart, although the smallest repeater module in a polymer, two AGUs shape a cellobial structure next to each other. The degree of polymerization (DP) reflects the number of AGUs in the polymer and the distribution of molecular vulnerabilities will greatly affect the properties of the fibers, since the volume of a single polymer is not homogenous. Cellulose-based polymer DP in wood cellulose may be up to 10,000 and even higher, for instance, in natural plant fibers in cotton. DP in wood cellulose has been decreased to approximately 300–1700 following decay reaction and purifying processes (Klemm et al, 2005; Kamel, 2007).

Thanks to the circular, relatively normal form of a cellulose and the several hydroxyl groups in the molecule, cellulose polymers may create complex crystalline configurations linked to hydrogen bonds. Some crystalline regions give the cellulose fibers important mechanical properties. Hydroxyl groups may establish the hydrogen links inside the cellulose polymer between numerous cellulose polymers or inside the polymer itself (Lennholm and Henriksson, 2007).

There are three distinct levels: the cellular, the supramolecular, and the morphological cellulose fiber form. Supramolecular forms are the polymer chains structured for specific hydrogen bonds in crystalline and non-cristalline regions, cellular fibers and walls are the morphological form (see Fig. 3.2).

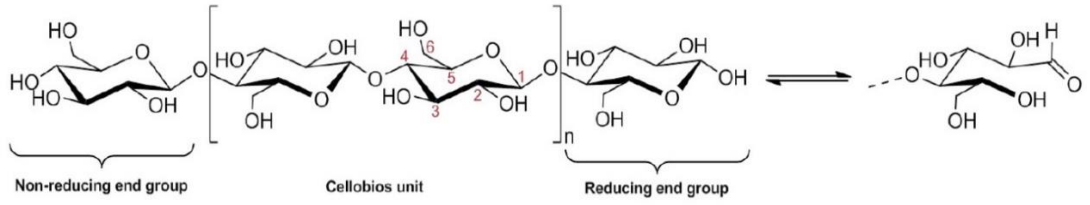


Figure 3.2 : The chemical composition of a cellulose polymer, the smallest repetitive element in the material, is the cellobios. The reduction ending unit can be either a free hemiacetal or an aldehyde (Börjesson and Westman, 2015).

The infinite natural resource and the primary source of recycled goods on an industrial scale is cellulose, one of the most significant natural polymers. The worldwide cellulose volume rises to 700 billion tons, but at the present, just 0.1 billion tons is used to manufacture pulp, textiles, medicines and other goods. The broad units called

primary fibrils, or microfibrils, which are formed of biomass and consist of around 36 individual cellulose molecules, are cellulose, hemicellulose, and lignin. Basic fibrils/microfibrils are bundled into bigger units known as microfibrillated cellulose. The hierarchical organization from the tree to the molecule of cellulose is shown Figure 3.3.

In addition to renewability and bio-degradability, the development of cellulosic fibers is bounded by promising properties such as high mechanical strength, hydrophilicity, widespread chemical modifications, the creation of flexible half crystalline morphologies, vast surfaces areas and weak density structures. The cellulosic source, situations, measurements, methods and functions of preparation can be modified. Thus, generally it is possible to categorize nanocellulose into three main groups.

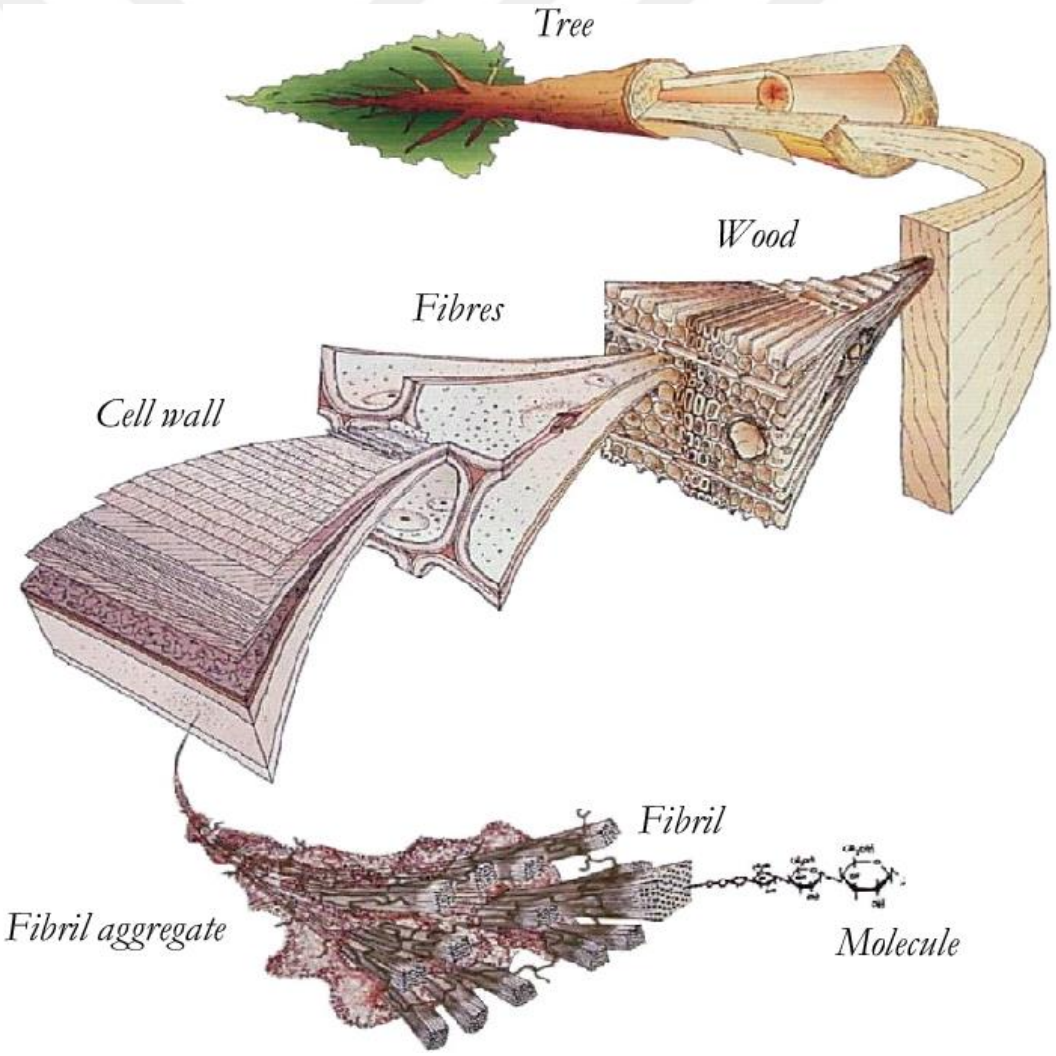


Figure 3.3 : Hierarchical organization, from the tree to the molecule of cellulose (Halonen, 2012).

Nanocellulose materials divided mainly three types which are:

- Nano/Microfibrillated cellulose (NFC/MFC),
- Cellulose nanocrystals (CNC),
- Bacterial nanocellulose (BNC).

General categories of nanocellulose is shown in Table 1. Nanocellulose is distinguished by strong mechanical strength, structurally configurable chemistry, higher aspect ratio, and biodegradability. Other significant fields of future usage are the sustainable green substrates for food processing, plastic coating and fillers and a lot of technologies for industrial applications.

Common types of nanocellulose is shown in Table 3.1 and detailed information is given for each type below.

Table 3.1 : Common types of nanocellulose (Julkapli and Bagheri, 2017).

Type	Sources	Productions	Particle Size	Example	References
Cellulose Nanocrystals (CNC)	Cellulose from algae and bacteria, wood, flax, cotton, hemp, mulberry bark, wheat straw, tunicin, ramie	Acid hydrolysis of cellulose from various materials	Diameter: 5 to 70 nm Length: 100 to 2500 nm	Cellulose nanocrystals, rodlike cellulose microcrystals, crystallites, whiskers.	(Liu et al., 2014)
Microfibrillated cellulose (MFC)	Flax, hemp, potato tuber, sugar beet, wood	Mechanical force before and/or during the application of chemical or enzyme delamination of pulp.	5 to 60 nm in diameter and micrometer range in length	Microfibrillated cellulose, nanofibrils, nanofibrillated cellulose	(Sorvari et al., 2014)

Table 3.1 (continued) : Common types of nanocellulose (Julkapli and Bagheri, 2017).

Type	Sources	Productions	Particle Size	Example	References
Bacterial nanocellulose (BNC)	Low molecular weight sugars and alcohols	Bacteria synthesize	Diameter: 20 to 100 nm	Bacterial cellulose, microbial cellulose, biocellulose	(Moritz et al., 2014)

3.2.1 Cellulose nanocrystals (cnc)

The acid hydrolysis is used to extract the amorphous parts from filtered cellulose nanocrystal (CNC) and then ultrasonic treatment applied. The exempt crystals derived from variable cellulose sources are determined primarily by the level of crystallinity. Depending on the biological sources CNC show different geometries (Dufresne et al, 2013). Examples of different geometries are has been deduced from electron micrographs of negatively stained ribbons in separate disaggregation conditions that intact ribbons are made of approximately 46 microfibrils, each approximately 1.6 x 5.8 μm and separated in two layers, such that the narrow directions of the microfibrils lie parallel to the thin ribbon axis. Broad bacterial cells about to split, and with an incipient furrow, had two ribbons reaching along one end (Brown et al, 1976).

Cellulose, hemicelluloses and lignin form the biggest part of cell walls in plants and lignin acts a bonding agent between hemicellulose and celluloses component consisting of 10-25% of dry weight (see Figure 3.4). With the support of binding mechanism, lignin in plant cell wall gives rigidity and strength. On the other hand, two other main cell wall components comprise around 35-50 and 25-35 percent by respectively cellulose and hemicellulose, by dry lignocellulose biomass (Sharma et al, 2018).

Cellulose is the linear polysaccharide and cellobiose units linked by β-1,4 linkage (Phanthong et al, 2018; Dufresne, 2012). There is also strong molecular bonding of adjacent glucose units in the same or different chain through hydroxyl groups in glucose monomer units. Plant cell walls primarily contain xylans and glucomannans, which are pentose and hexose monomers and are connected together by thin or transient chains (Phanthong et al, 2018; Dufresne, 2012).

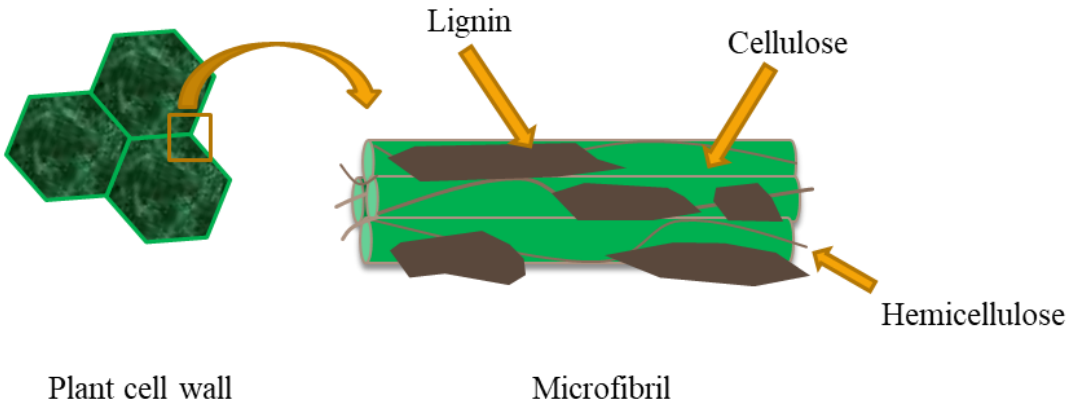


Figure 3.4 : Structure of a plant cell wall formed by lignin, hemicellulose and cellulose (Redrawn with permission, from Sharma et al, 2018).

The versatile hydrogen bonding system guarantees various properties of the cell wall of the plant, such as antibacterial properties, durability and strength, water or solvent insulative properties, etc. (Sharma et al, 2018).

3.2.2 Nanofibrillated cellulose (nfc)

Cellulose nanofibrils (CNFs)/Cellulose microfibrils (CMFs), are unlike CNC generated through mechanical treatment that retains the microfibril's non-cristalline sections and the duration of the fibrils. Microfibrils are small, thread-like bundles of cellulose molecules that are bound to hydrogen bonds in cellulose polymers, often about several hydroxyl groups. Forces will remove the fibers using physical treatment, and the interfibrillary linkages between the cellulose molecules will break and deliver nanofibrils with a nanodimensional diameter and fiber width ranging between nanometer to micrometer (see Figure 3.5).

Typical mechanical procedure for CNF is the grinding of the pulp accompanied by homogenization of the nanofibrils and the smooth dissipation of the pulp when mixed with water (Börjesson and Westman, 2015). CNF may come from many different forms of sources of cellulose. A significant field of focus for CNF is in applications including composites where the large CNF aspect ratio and large compact microfibrils are suitable for use in polymer matrix strengthening applications. Bhatnagar and Sain researched cellulose nanofibers in plants due to wide availability and low expense (Bhatnagar and Sain, 2005).

Until its use as a filler in the PVA matrix, CNF was processed from rutabaga, kraft pulp, flax fibres, and hemp fibers using chemical-mechanical techniques.

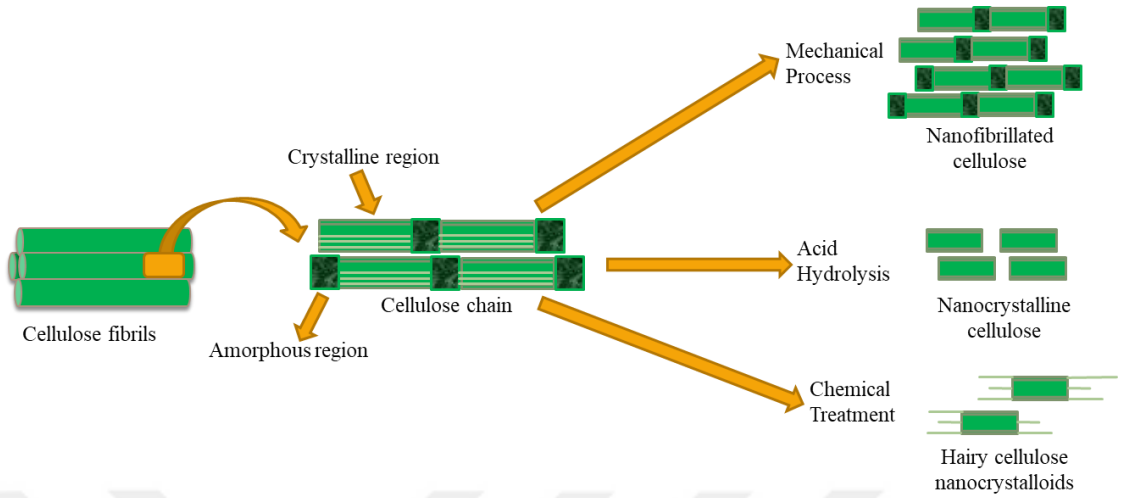


Figure 3.5 : Schematic description of the separation of nanocellulose from lignocellulose biomass (Redrawn with permission, from Sharma et al, 2018).

Compared to flat PVA, the usage of plant fibers as supports in composites has improved the structural properties of the composite substance (Börjesson and Westman, 2015; Bhatnagar and Sain, 2005).

3.2.3 Bacterial nanocellulose (bnc)

The literature about BNC and its layout and properties includes many articles and analysis papers (Kamel, 2007; Börjesson and Westman, 2015; Klemm et al, 2011; Klemm et al, 2006). Compared to other forms of cellulose, bacterial cellulose is formed in nanofibers by a particular bacteria named Acetobacter, which is grown in a culture medium. The microbiota generate BNC through the synthesis of cellulose and the formation of microfibril bundles (Kamel, 2007; Börjesson and Westman, 2015; Klemm et al, 2011).

Acetobacter is a microorganism present anywhere in life where the fermentation of sugar takes place and is involved in the transition of ethanol into acetic acid. For several years, acetobacter is used in the fermentation industry for the industrial processing of acetic acid and is used in several other sectors where acetic acid is essential (Börjesson and Westman, 2015).

3.2.4 Nanocellulose extraction process

3.2.4.1 Pretreatment of biomass for extraction of nanocellulose

The extraction of nanocellulose starts with the removal of hemicellulose and lignin from the key cellulose unit. Alkali and acid-chlorite treatment are the major approaches (Phanthong et al, 2018; Klemm et al, 2011).

Alkali treatment

Biomass is primarily processed with potasium and sodium hydroxide to extract the amorphous area of lignin and hemicelluloses from the cellulose of fibers. In order to neutralize the purified solid portion, it is washed with water and the solid component is mainly formed by cellulose (Sharma and Mandal, 2017).

Acid-chlorite treatment

The combined process is used to remove lignin from lignocellulosic biomass by acidifying sodium chlorite with acetic acid. This method is referred to as the whitening or delignification procedure. Distilled water combined with acetic acid and sodium chlorite with lignocellulosic biomas for roughly 4-12 h at 70-80 ^{o}C (Santos et al, 2013; Phanthong et al, 2015). Following a night of stirring lignocellulosic biomass wash with purified water approaches a neutral pH level. Residues obtained and dried in the oven at 50 ^{o}C and identified as lignin-free holocellulose.

3.2.4.2 Isolation methods of nanocellulose

The separation of nanocellulose can be accomplished by three distinct processes, such as acid hydrolysis, enzymatic hydrolysis and mechanical treatment.

Acid hydrolysis

Acid hydrolysis is a process widely used for the separation of nanocellulose. Primary hydrolyzing of amorphous areas of cellulose fibroids through esterification of hydrosphorous groups using sulfate ions are heavy acids such as acetic acid, formic acid, sulfuric acid, chlorine oxide, phosphoric acid etc. At the end of the reaction, crystalline region of cellulose fibers change their forms from amophous to stable colloidal dispersion (Xie et al, 2018). The reaction of acid hydrolysis depends on three main factors, such as temperature, reaction time and acid concentration, which affect

the final properties of the cellulose produced. Cold water followed by sodium hydroxide or centrifugation is usually used to regulate pH in neutral conditions (Sharma et al, 2018).

Enzymatic hydrolysis

Enzymatic hydrolysis is another way of isolation method for nanocellulose. It can be defined as a kind of biological treatment for obtaining washed cellulose including ezymes for modification or digestion of cellulose fibre. Cellulase, endoglucanase, cellobiohyrolase are mostly used enzymes mentioned in the literature. The enzyme activity is mainly focused on the fracture/catalysis of the H-bond connection between cellulose microfibers. Hemicellulose hydrolysis is essential for both the processing of hemicellulose from hydrolysis to cellulose, and the generation of hemicellulose monosaccaharides for further fermentation into bioethanol (Phanthong et al, 2018; Xie et al, 2018).

Mechanical process

Specific mechanical techniques for the mechanical isolation of cellulose fibers, such as ultrasonics, high-pressure homogenization and ball milling, are the most frequently quoted in the literature (Phanthong et al, 2018; Klemm et al, 2011). While certain pre-treatment procedures have been undertaken to minimize energy intake, the main drawback of such processes still involves high energy intake.

Nanocellulose extraction methods are illustrated and there are a number of production units based in the USA and Canada, Europe and Asia. TThe most commonly known approach in the nanocellulose crystal and nanocellulose fiber insulation industries is acid hydrolysis + mechanical method (Phanthong et al, 2018).

3.2.5 Bacterial nanocellulose extraction

Cellulose fibers may be generated from plants as a natural source, instead cellulose fibers can also be developed as extracellular biosynthetic products from other bacteria belonging to the genera Acetobacter, Alcaligenes, Pseudomonas, Agro bacterium, Rhizobium, or Sarcina. According to the literature, the most effective source of bacterial cellulose is the Gram-negative form of the bacteria containing acetic acid, Acetobacter xylinum (or Gluconacetobacter xylinus). Bacterial cellulose is generated by cellulose biosynthesis and collected in the form of ribbon-shaped fibrills less than

100 nm in width and far finer in size up to 2–4 nm in nanofibrills (Wahlström and Suurnäkkia, 2015). Similar to the CNC situation, a method of acid hydrolysis may also be used to transform BNC microfibrils into bacteria nanocrystals (Phanthong et al, 2018).

3.2.6 Application of nanocellulose nanocomposites

Bionanocomposites dependent on cellulose have many diverse uses in various industries. In paper and packaging industry nanocellulose and its biocomposites have potential applications.

Potential applications of paper and packaging industry is listed in Table 3.2 according to the production volume and novel/emerging applications.

Nevertheless, nanocellulose gained considerable attention owing to its nanoscale aspect, its strong strength and stability properties from several sectors, such as building (in the area of structural composites), automobile (manufacturing components centered on micro-patterns), electronics, cosmetics and pharmacy. Additionally, nanocellulose composites have the potential to use as membrane for ion exchange, ultrafiltration, fuel cells etc.(see Fig. 3. 6) (Phanthong et al, 2018).

Table 3.2 : Potential application field of nanocellulose in paper and packaging industry.

High volume applications	**Low volume applications**	**Novel and emerging applications**
Packaging coatings	Aerospace interiors	Air filtration
Paper coatings	Aerogels for the oil and gas industry	Viscosity modifiers
Paper filler	Paint – architectural	Purification
Packaging filler	Paint – special purpose	Cosmetics
Replacement–plastic packaging	Paint – OEM applications	Excipients

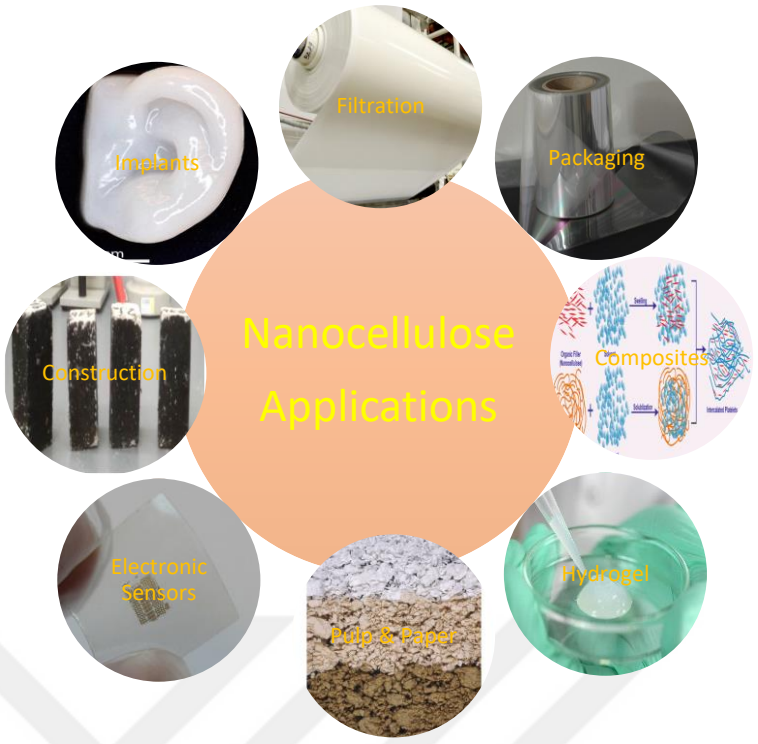


Figure 3.6 : Potential uses of nanocellulose in diverse areas.

3.2.6.1 Composites and fillers

Recent work has oriented on developing methods for the development of polymeric nanomaterials based on natural fillers with strong stability and dissipation between reinforcement and matrix. Various important informations can be found in the works of (Dufresne, 2012a; Dufresne 2012b; Siqueira et al, 2010; Ferreira et al, 2018). Composites can be developed using three specific techniques: casting method, melt mixing, and in situ polymerization.

Different thermal and mechanical performance can be obtained depending on the method. For instance, Wang et al. (2019) have researched the effect of the preparation process on the final output of bamboo pulp fiber (BPF)/HDPE composites. Crystallinity index and heat distortion temperature display difference depending on the method used, according to the study results of E' (Ferreira et al, 2019). Nanocellulose applications as a reinforcing agent mentioned by Nakagaito and Yano (2008) for phenolformaldehyde resin coupled with cellulose nanofiber. In fact, Zimmermann et al. (2017) also observed identical findings with hydroxypropylated cellulose. The results mainly indicates the addition of 1% of cellulose nanofibers, cell density signifcantly reduces when compared with the pure EVA foams. Henriksson and

Berglund (2007) stated in recent literature that nanopaper was impregnated with melamine formaldehyde (MF).

3.2.6.2 Paper and packaging industry

Techniques are often utilized by the paper and packaging industries to reduce the usage of petrochemical artificial polymers incomparison with nanocellulose (Lavoine et al, 2012). Nanocellulose has certain excellent properties, such as nanoscale proportions with gas and water barriers, which can be efficiently used to extend nanocomposite film with a strong building network for molecular penetration (Nair et al, 2014). Nanocellulose can also produced from a sustainable source of natural polymer cellulose, which is also of a cost-effective, non-toxic type and is highly desirable use in food packaging. Recently, it has been reported in the literature that a nano-biocomposite film has been developed for the application of food product packaging, along with a nanocellulose and polylactic acid matrix with nanocellulose as a binding agent, resulting in substantial improvements in the properties of water and oxygen barriers (Trifol et al, 2016). Composites with 1 or 5 wt% of nanocellulose, in combination with 1, 3 and 5 wt% of nanoclay, were prepared, and their barrier properties were investigated. It was found that the combination of clay and nanocellulose clearly resulted in synergistic behavior in terms of the oxygen transmission rate (OTR) through a reduction of up to 90% in OTR and a further reduction in the water vapour transmission rate of up to 76% (Trifol et al, 2016). Carboxymethyl guar (CMG), poly(vinyl alcohol)/polyacrylamide agar or semi-interpenetrative polymer network can also be used as a matrix for the processing of nanocellulose composite films, such as improved polymer gas filter and mechanical packaging features (Sharma et al, 2018).

3.2.6.3 Electronics industry

Nanocellulose composite films can be used in another important field, such as the electronics industry, due to their increased conductivity and robustness. For example, polyaniline nanocellulose composite films are mostly studied in literature for various end-use applications in electronic fields such as paper-based sensors, electronic devices, adhesive conductors and flexible electrodes (Tammela et al, 2015; Wang et al, 2014a; Wang et al, 2014b; Zhang et al, 2013). Nonetheless, electrodes may be produced from polypyrol composites, nanocellulose and carbon filaments, as reported

by Razaq et al. (2012) for the efficient use of discharge power and high loads, high cell efficiency and cycling performance paper-based energy storage devices (Wang et al, 2014a; Wang et al, 2014b). Charge capacities of more than 200C g−1 (PPy) are obtained for paper-based electrodes at potential scan rates as high as 500 mV s−1, whereas cell capacitances of ~60–70 F g−1 (PPy) are reached for symmetric supercapacitor cells with capacitances up to 3.0 F (i.e.,0.48 F cm−2) when charged to 0.6 V using current densities as high as 31 A g−1 based on the PPy weight (i.e., 99 mA cm−2) (Razaq et al, 2012).

Flexible organic electronics with thin membranes of uncoated poly(3,4) ethylenedioxythiophene and bacterial nanocellulose can be produced with good electrical conductivity (Müller et al, 2016).

3.2.6.4 Biomedical applications

Nanocellulose with certain special properties, such as high surface-to-volume ratio, strong intensity and improved surface chemistry, has often been used in biomedical fields (De France et al, 2017; Mandal and Chakrabarty, 2017). Main topics of nanocellulose use in biomedical applications can be summerized under following titles:

- Tissue bioscaffolds for cellular culture
- Drug excipient and drug delivery
- Immobilization and recognation of enzyme/protein
- Substitutes/medical biomaterials
- Blood vessel replacement
- Sof tissue-ligament, meniscus, and cartile replacements
- Nucleus pulposus replacement (Lin and Dufresne, 2014).

Sampath et al. (2017) recently confirmed the existence of an innovative hydrogel with a semi interpenetrating polymer matrix that improved the pH response and mechanical properties to be used for novel pharmaceutical and gene transfer implementations.

Recently another research article stated that electrospun poly (ϵ-caprolactone)/nanocellulose composite fiber mat was created to be used as a scaffold for tissue engineering applications (Si et al, 2016).

3.2.6.5 Filtration/purification applications

Due to the growing emphasis in renewable growth and nanotechnology, the usage of CNCs in water treatment applications has gained rising popularity. Cellulose Nanocrystals are suitable candidates as they have a large specific surface region, excellent resilience, hydrophilicity, biodegradability and surface versatility (Peng et al, 2011). Organic dyes, pharmaceuticals, heavy metal ions, pesticides, PAHs and biomolecules are among the major forms of pollutants found in water bodies. Conventional adsorbents may be energy consuming and toxic as well as produce greenhouse gaseous chemicals, such as activated charcoal. This also provides many different possibilities for the manufacture of alternative low-cost adsorbents from industrial and agricultural by-products (Ali and Gupta, 2007; Bhatnagar and Sillanpää, 2010; Crini, 2006). By utilizing green nanomaterials, such as Cellulose Nanocrystals, our dependency on activated carbon can be kept as low as possible and the carbon footprint can be minimal (Batmaz et al, 2014; Mohammed et al, 2015; Grishkewich et al, 2017). There are several literature studies done about adsorption capacities of cellulose nanocrystals such as petroleum products fabrication of cellulose nanocrystals based ultra-porous aerogels for water/petroleum mixtures (Korhonen et al, 2011), pharmaceutics adsorption studies for extracted CNCs from green seaweed modified by acid hydrolysis were shown successful resuts removing tetracycline hydrochloride from aqueous solutions (Rathod et al, 2015), another area using CNCs as adsorption material is biomolecules adsorption (Demirci et al, 2014), small organic molecules called non-dye molecules such as chlorinated phenolic compounds from wastewater, and another commonly use areas of CNCs are removal of heavy metals (Yang et al, 2008), and removal of textile dyes (Song et al, 2017; Jin et al, 2015).

Discription of a nanocellulose membrane for water purification was electrospun mats of functional nanocellulose (Ma et al, 2012a; Rathod et al, 2015; Akhlaghi et al, 2014). Impregnation of electrospun mats of various appearances levels with nanocrystals has revealed the potential, depends on the volume of the electrospun surface impregnation, to process the charge micropores with isotropically or anisotropic structures (Ma et al, 2012b; Ma et al, 2011; Goetz et al, 2011). Application of CNC to an electrospun nanospun nanofiber polyacrylonitrile (PAN) scaffold and composite heating at 100 °C for 10 minutes to connect Cellulose Nanocrystals (CNC). This flexible technique was used to create mechanically solid composite nanofiber membranes (Akhlaghi et al,

2014). Akhlaghi. (2014) showed that the electrospun nanofibrous membranes of CNC could effectively extirpate with a fairly large and low concentration between two bacteria (ie., Brevundimonas diminuta, and Escherichia coli) and one form of virus (i.e. Bacteriophage MS2) (Ma et al, 2011; Wang et al, 2013; Voisin et al, 2017). In the study Ma et al. (2012) used a composite nanofibrous membrane (electrospun PAN on PET nonwoven) in the form of a disk sample with a diameter of 25 mm in a dead-end filtration cell. 0.1 g cellulose nanowhisker aqueous suspension (0.4 wt% concentration, pH 7.0) is gradually infused into the membrane disk by gravity and the membrane disk was subsequently heated to 100 ^{o}C for 10 min to cross-link to cellulose nanowhisker network.

In addition to these successful manufacturing strategies, the electrospinning method for the development of nanofiber membranes has evolved as an important technology for the development of robust and future water treatment membranes and enhanced desalination. Figure 3.7 reveals some significant advantages of the electrospinning technique and the potential for generating the required electrospin nanofiber membranes.

3.3 Fiber Spinning

The processing or fusion of polymer solutions into micro or nanofibers is not a new electrospinning technique. William Gilbert's first experiments date back about 400 years to the 17th century. A water droplet is attracted to a conical formation on a smooth and dry surface while a fragment of rasped amber is kept at a point. Theoretical research persisted between the 17th and the 20th centuries and, in 1969, Taylor found that fluid conducting would occur in equilibrium as a cone, if the semivertical angle is 49.3 degrees, under the influence of an electrostatic field. When electrical field is applied to a drop of liquid electrical field, pulled into a spheroidal shape untill a critical value of $1.62(T/r_0)^{1/2}$ and the droplet becomes 1.85 times longer than the equatorial diameter.

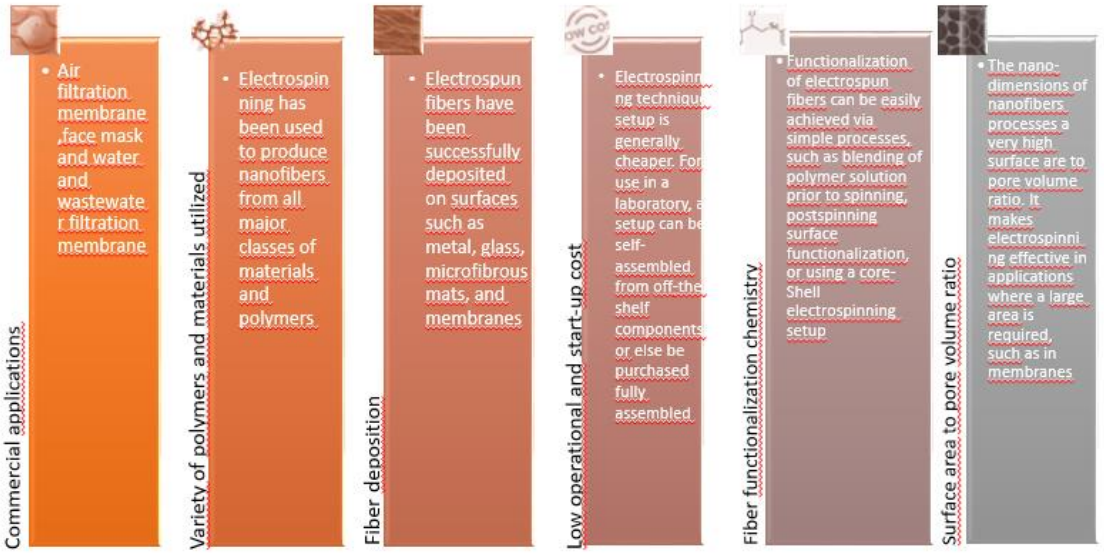


Figure 3.7 : Specific features of electrospinning techniques used for the manufacture of membranes that allow for a large surface-to-volume ratio, the use of various polymers and materials, low start-up costs, fiber deposition on other substrates, fiber functionalization and industrial applications (Ray et al, 2018).

Electrostatic units for electrical field and centimeter-gram-second (C.G.S.) units for surface tension (dyne/cm) and r_0 for the initial Radius. The conical form of the electrospinning jet was referred to as the "Taylor cone" in later literature.

Important milestones of the electrospinning technology is shown in Fig. 3.8**.**

The jet loop is thinner and longer than it is put on the collector plate, which is a required distance away from the spinner. As the jet exits the spinneret, the loop width and the diameter of the circle continue to increase. The fluid uncertainty can be summed up in three phases as listed below (Renekar et al, 2000):

- A straight section of the jet may grow a variety of curves or encounter curvilinear motion during the starting stage of the electro-spinning cycle.
- There are a variety of spiral and whipping circles with increasing radii that will lengthen the segment of the jet in the curve.
- As the width of the loops increases, the width of the fibrous jet may become smaller. Small scale fibrous jet lead to start of the next cycle of bending instability.

Nanofibers (or conditions-based micron and submicron fibers) need to be formed and replicate themselves many times in a bending process. Due to the natural convection

process, the solvent evaporates and leaves a nanofibrous mat on the collector screen (Renekar et al, 2000). Figure 3.9 shows all steps for the fabricationof a nanofiber mat.

3.3.1 Background

Polymer nanofibers of varying diameters ranging between 2 nm to a few micrometers from various traditional polymer technologies can be developed by electrospinning. In order to fabricate nanofibrous materials, many essential factors that may have a major impact on the formation and structure. These parameters are known as (a) solution parameters, (b) process parameters, and (c) ambient parameters (see Fig. 3.10) (Ray et al, 2018).

Electrospinning is the most effective method for the manufacturing of nanofibrous materials. One of the most significant benefits of utilizing this method is fast speed, low cost, flexibility and extensive choice of materials. Fiber morphologies and microstructure of electrospinning process is significantly affected from operational parameters (Aussawasathien et al, 2008; Shao et al, 2004).

3.3.2 Polymer solution parameters

3.3.2.1 Concentration of polymeric solution

The concentration of the polymer solution during the formation of nanofiber plays a crucial role. Following crucial measures reported as the concentration of polymer solution rises from small to high:

- In extremely small concentrations of polymer electrospraying usually occurs rather than electrospinning owing to small viscosity and high surface tension of the polymeric solution.
- A slight increase in the concentration of polymers is caused by a combination of bead and fiber bubbles.
- Smooth nanofibers that can be produced when the strength of the polymer meets the optimal point.
- Since the polymer is very small, microribbons in the form of a helix are observed (Eda and Shivkumar, 2007; Fong et al, 1999; Lee et al, 2003; Li and Wang, 2013).

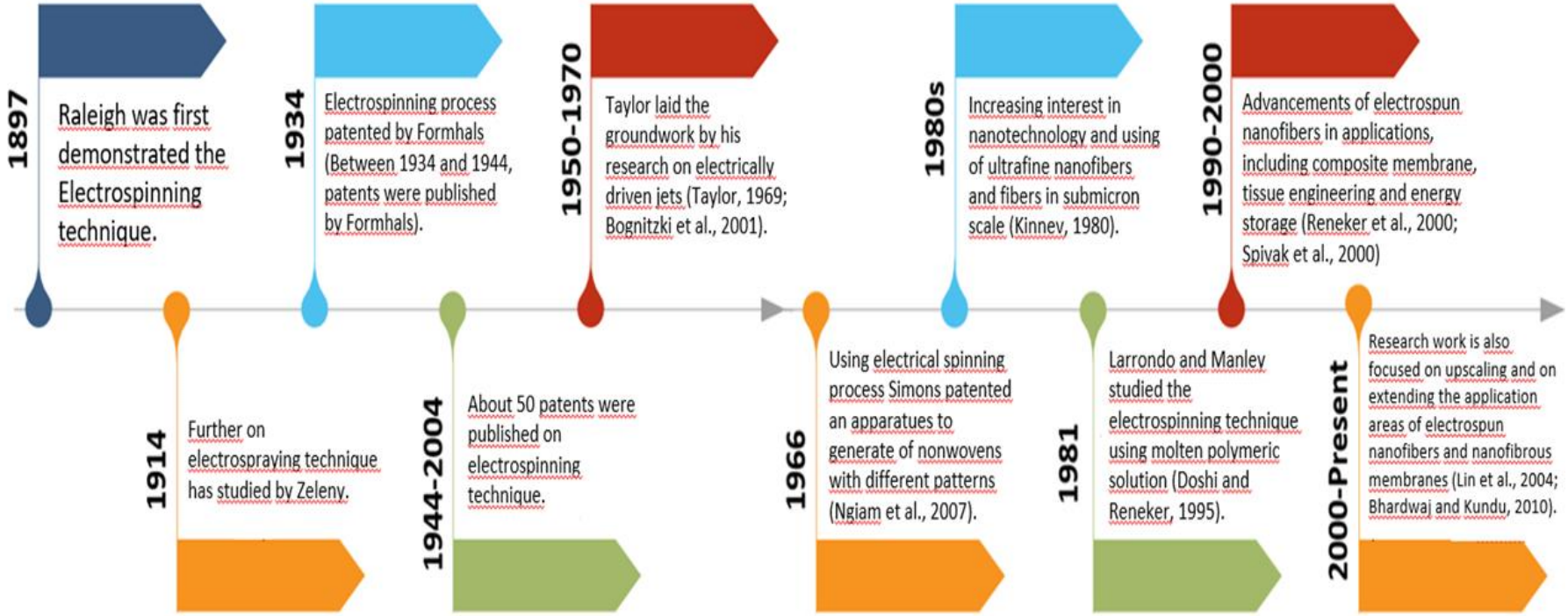


Figure 3.8 : Important milestones in electrospinning technology.

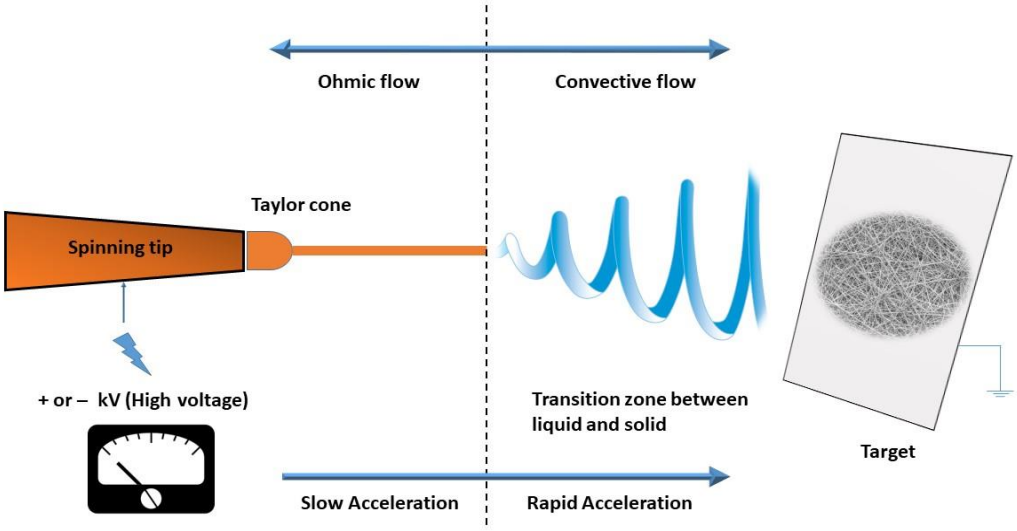


Figure 3.9 : Basic experimental structure of the method of spinning.

a)Solution Parameters	b)Processing Parameters	c)Ambient Parameters
• Solution Concentration • Molecular weight of the polymer • Viscosity • Surface tension • Solvent properties • Conductivity	•Applied voltage •Distance of the electrode from the collector •Flow rate •Capillary geometry	•Temperature •Relative Humidity

Figure 3.10 : Process improvements made by controlling these parameters have contributed to the development of smooth, nanofibrous membranes (Dietzel et al, 2001).

3.3.2.2 Concentration of polymeric solution

The microstructure and configuration of electrospun nanofibers have an effect on the molecular weight of the polymer. In particular, the polymer's molecular weight represents the degree of entanglement in the solution between the polymeric chains. When the molecular weight of polymers with a large degree of hydrolysis reduces, the viscosity of the solvent rises considerably such that the fluid content remains constant. If the molecular weight decreases, it is also necessary to reduce the solvent evaporation from the gel-form (Koski et al, 2004).

3.3.2.3 Viscosity

Determination of the microstructure and composition of the fibers for the viscosity of the solution is important. According to the studies, consistent and seamless nanofibers could not be made from polymer solutions with very low to very high viscosity. Thus, always an optimum viscosity need to find for electrospinning (Larrondo and St John Manley, 1981). As stated before the viscosity of the solution, the concentration of polymers and molecular weight are linked to each other.

The polymeric solution will reach the necessary viscosity to be added to nanofibers used for electrospinning. Usually, the entanglement quantity of a polymeric solution may be used in electrospinning techniques to examine the forming of nanofibers. The entanglement number can be described mathematically as follows:

$$(\mathrm{ne})\mathrm{solution} = \frac{\mathrm{M_w}}{(\mathrm{Me})\mathrm{solution}} = \frac{\phi \mathrm{p}.\mathrm{M_w}}{(\mathrm{Me})} \quad (1.1)$$

ne: The entanglement number,

Mw: The molecular weight,

Me: The solution entanglement molecular weight, and

ϕp : The polymer volume fraction.

Studies have shown that if polystyrene, polyethylene oxide polymer, polylactic acid and are used in an appropriate solvent, the entanglement number is higher than 3.5, which allows the creation of smooth nanofibers. If the entanglement number is about 2<ne<3.5, a mixture of beads and nanofibers is generated and for ne<2 no fibers are created (Ray et al, 2017a; Ray et al, 2018).

3.3.2.4 Surface tension

The solvent content of the soluton is an essential aspect of surface tension. Different solvents can lead to various surface stresses. At a specified concentration, a decrease in surface tension will create clean nanostructures from polymeric solutions. Latest research indicates that the texture and viscosity of the solution can be changed by adjusting the mass ratio of the solvent mixture (Shenoy et al, 2005). Using various surfactants, final electrospun polymeric nanofibrous membrane may introduce impurities. Not only decreased surface tension, but also added additional charging

carriers to the solutions that increased nanofibers efficiency are anionic surfacants such as sodium dodecyl surfate (Shenoy et al, 2005; Ray et al, 2017b).

3.3.2.5 Surface charge density and conductivity

Polymer and solvent type of the solution have significant affects on conductivity. The natural polymers are polyelectrolytic materials. Under an electrical field of low charge intensity in a polymeric solution leading to higher surface tension resulting in poor-quality nanofibers. In addition, the introduction of ion salts like KH_2PO_4 and NaCI will create a consistent fiber diameter (Zong et al, 2002; Huanf et al, 2006). The electrical conductivity may be improved by the addition of organic acid as a solvent (Ray et al, 2016).

3.3.2.6 Solvent volatility

Solutions formulated with very low volatility solvents could have created wet and fused nanofibers or even negligible nanofibers. On the other hand, polymer solidification may happen at the spinneret tip if we use a highly volatile polymeric solution resulting intermittent spinning (Mit-uppatham et al, 2004a; Mit-uppatham et al, 2004b).

3.3.3 Process parameters

In order to fabricate smooth and fine fibers via electrospinning process parameters are very crucial.

3.3.3.1 Applied voltage

Threshold voltage is crucial forming jets ejected from the Taylor cone. It's not certain that diameter of electrospun nanofibers effected positive or negative direction. Reneker and Chun concluded that electrospun polyethylene oxide (PEO) does not change the diameter of the fibers under 1.5×10^{-7} m^2 V^{-1} s^{-1} (Reneker and Chun, 1996). At the other side, other studies have shown that higher voltages contribute to greater fiber diameters (Chang et al, 2016). Some researchers have indicated that the change in the applied voltage raises the electrostatic repulsive force of the fluid polymer flow, which essentially facilitates the tightening of the fiber diameter. For certain situations, though, improved columbic forces and a stronger electrical field for the jet lead to greater voltage stretching. Improved electric field and strong solvent

evaporation decrease fiber diameter. Higher voltage (typically around 10 kV–20 kV) has the potantial of beads formation. The degree of the output is calculated by the concentration of polymer solutions and the gap between the tip and the collector (Chang et al, 2016; Yördem et al, 2008).

Upon dissolving in suitable solvents, most polymeric solutions may be electrospun between 7 -30 kV. Nonetheless, in order to generate nano-sized fibers, the electrostatic field applied would be greater. If the polymer solution becomes charged by electrostatic force, further pressure is introduced into the polymeric solution and repulsion of reciprocal charges produces longitudinal stresses. The polymeric solution improves its quality. In addition to the applied stress, the positive and negative ions move in the opposite direction as the atmospheric electrostatic pressure is applied to the polymeric fluid. Negative ions generally migrate in the direction of a positive interface electrode. The disparity between the amount of positive and negative ions is regarded as the excess voltage, or simply the energy. Salt may be applied to the polymer solution to allow electrospinning for polymer solutions that are isolating. The solution is built with an electrically charged jet with a surplus charge as the electrostatic energy is applied (Renekar et al, 2000).

3.3.3.2 Feed flow rate

The flow rate influences the direction of the jet and the rate of materials movement. A relatively lower feed rate is more desirable because the solvent would have more duration to evaporate. Each spinning solution has its own optimum flow rate. Data has shown that polystyrene (PS) fibers are growing in their diameter and pore diameter as the polymer flow rate increases. A tuning of the flow rate can alter the morphological structure slightly. A large difference in the values of the solubility parameter and in the dielectric constant of PS and a solvent induced the formation of a bead-on-string morphology. The productivity of the as-spun fibers increased with increasing dielectric constant and dipole moment of the solvents. Well-aligned, uniform electrospun fibers of PS can be produced from DMF solution using a rotational speed of the collector of 1500 rev min^{-1}, under an applied potential in the range of 15–20 kV, and with the nitrogen feeding rate as low as possible (Wannatong et al, 2004).

3.3.3.3 Collector types

Electrospinning process effected by collector used in the system. In this process, nanofibers are collected on a conductive substrate. Aluminum foil is commonly used as a collector, but other collectors include conductive paper, bar grid, conductive cloth, pin, parallel bar, revolving roll, wire mesh, spinning wheel, liquid anti solvent such as a methanol coagulation bath and many more (Kumalo, 2012). Wang et al. (2005) used two forms of aluminum foil collector and wire screen, and found that the processing of fiber was adversely influenced by the usage of wire screens due to a less conductive field. Less surface area cause bead generation of on fiber fabrication. For another analysis the aluminum foil and aluminum foil wire displays for the same electrical area were contrasted and pure wire display was showing better results for fiber selection because fiber transition to another substratum was made possible with the use of wire screen. By determining of the rotation speed and the type of the targe/collector fiber alignment is ensured. Thanks to the elastic bending of the strongly charged jet, nanofibers are located arbitrarily on the collector. Studies have shown that, in order to be more or less adjacent to each other, the usage of revolving drums or a spinning wheel-like bobbin or metal frame as a collector provides stronger performance.

3.3.4 Tip to collector distance

The distance between the tip and the collector is among the most popular ways to supervise fiber thicknesses and structure of electrospinning. Researchers found that the fibers require minimum distance before entering the collector to enable them to dry long enough. If there isn't enough distance, the fibers can be placed too close or too far from each other, and beads formation can also be seen. As with other variables, the role of the tip on the distance of the collector is not significant. Close distances may be given from flat fiber, where rounding fibers with spinning velvet-like polymer with fibronectin functionality are observed at a fairly wide distance. For example, if it is desired to form smaller fibers with polysulfone polymer, close distances should be preferred. Another significant problem concerning the structure of nanofibers created by electrospinning is to leave the gap where the solvent used to disperse the polymer will evaporate and the fibers stay dry. The optimal gap must therefore be changed to evaporate the solvent and hold fibers dry.

3.3.5 Ambient parameters

Other parameters such as humidity and temperature are critical for polymer electrospinnig, based on the process and solution parameters. Several studies were conducted to investigate the impacts of atmospheric parameters on the electrospinning cycle. Mit-Uppatham et al. (2004) studied the temperature impact between 25-60 °C on the electrospinning of polyamide-6 fibers. Researchers find that temperature rises, fiber yields are reduced with fiber diameter. At higher temperatures, they related this reduction in diameter to reduce the viscosity of the polymer solutions. Viscosity and temperature is inversely proportional.

Differences in humidity have been observed when spinning polystyrene solutions and findings indicate that circular structures developed on the surfaces of the fibers (Casper et al, 2004). On the other side, the volatile solvent will dry easily at very low humidity, as the solvent evaporates more rapidly. The evaporation rate is sometimes as high as the solvent extracted from the needle end. Researchers also suggested that high humidity may lead to electrospun fibers' discharge. In addition to solutions and processing conditions, the climatic conditions also affect the method of electrospinning.

3.4 Electrospinning of Nanocellulose

In addition to a theoretically simple and flexible process, electrospinning provides several more potential rewards from the perspective of fiber preparation in relation to NC (Teo and Ramakrishna, 2006). During the electrospinning process large electrostatic fields and cuts in fluid jet forces excite compatibility of the polymer chains and NC. The strong isolation also leads to the alignment due to its very low fiber diameter (Dong et al, 2012). Due to the very fine fiber diameter of the plane, solvent removal is very simple. This is capable of quickly locking the high polymer and nanocellulose alignment and avoids longer drying preriods which can lead to a relief in the middle of bigger fibers spread by other processes (Torres-Rendon et al, 2014).

Spongy polymer sheets of up to 50% NC have been electrospun, yet much smaller amounts are more common. The fact, partly, that the large increased viscosity with added CNF makes electrospinning harder and tends to result in larger fibers of the

diameter has almost exclusively used CNC as the NC components. A variety of polymers were tested as matrices (Clemons, 2016).

For example, CNCs have been added to clear polymers such as polystyrene Rojas et al. (2009) and poly(methyl methacrylate) Dong et al. (2012) in order to increase efficiency in implementations where opacity is important. A 100-percent bioassorted composites can be made utilizing bio-based polymers such as poly(lactic acid) Liu et al. (2011) and cellulose acetate (Herrera et al, 2011; Vallejos et al, 2012; Sun et al, 2015). The application of NC to biocompatible polymers (e.g., poly(μ-caprolactone) Zoppe et al. (2009), polyacrylic acid Lu and Hsieh (2009), poly(ethylene oxide) Park et al. (2007); Motaung and Mokhena (2015), poly(vinyl alcohol) Sutka et al. (2013); Lee and Deng (2011); Medeiros et al. (2008); Sutka et al. (2014); Peresin et al. (2010a); Peresin et al. (2010b) to have positive effects for medicinal use on electrospunic mats (e.g., tissue technology).

CNCs are applied to poly(vinylidenefluoride-co-hexafluoropropylene) by growing and reducing the pores for membrane distillation of pressed electrospun mats (Lalia et al, 2014). Polymer mixtures were also investigated (poly(vinyl alcohol)/lignine blends) (Ago et al, 2012). In addition, all cellulose composites were electrospuncturized by combining CNCs with CA, and then by alkaline hydrolysis, the acetyl groups were separated by the spun sheet. Many also demonstrated how compact CNC-inorganic particles migrate in magnetically activated mattresses, that can potentially be used in separation applications, can electrospun with polyvinyl alcohol (Dong et al, 2012). Adding NC to polymers causes a number of rotational results. It can improve the electrospinning solution's conductivity (for example, because it can lower the fibre diameter of negative charges on the unmodified CNC sulfate groups) (Peresin et al, 2010b).

Most of the research centered on the mechanical properties enhancement results of CNC. Effects are generally calculated by measuring the electrospun mat instead of the fibers themselves, since the mat properties are typically of considerable importance and are therefore simpler to do. The effect of the mixture of substrate behavior changes (e.g. polymer reinforcement, nuculation, or matrice crystallization inhibition) and matt surface structure (e.g. fibre alignment, porosity) and interface gumming are therefore due to these improvements.

Others showed significant implications for mechanical properties of CNC-added electrospun mats, particularly for biocompatible polymers and/or water-soluble matrices. It can be helpful in medicinal implementations where adjustments in material properties are sometimes needed. Electrospun mats are more cost-effective (Clemons, 2016).

Numerous methods to facilitate the alignment of nanofibers to generate directed fiber mat with better directional properties have been explored (Teo and Ramakrishna, 2006). For example, oriented PMMA mats with a collector with up to 41 percent CNCs (Dong et al, 2012). To CNC composites with a PVOH matrix, Lee and Deng (2011) used a similar approach. Another study was made using two metal sheets that were insulated from each other to align the composite fibers of their cellulose acetate (Herrera et al, 2011).

3.5 Conclusions and Future Perspectives

Electrospinning is an ordinary, special, versatile and economic technique that is commonly used for the processing of high-porosity, high-surface nonwoven fibers. Different parameters such as polymer content, molecular weight, viscosity, tip-to-collector gap, applied pressure, and solvent have a significant effect on electrospun nanofiber morphology. The electrospun nanofiber scaffolds for the desired function can be easily manufactured with control of these parameters. Nanofibers have identified various practical applications in almost any arena, including filtration, enzyme immobilization, membrane sensing cosmetics, affinity membranes, protective clothing, tissue engineering, drug delivery etc.

On the other hand, cellulose is the world's most plentiful natural material and an nearly infinite source of eco-friendly and bio-compatible goods. Cellulose-based products have therefore become in the 21st century one of the most significant bio-resources. Cellulose's single hierarchy enables the separation of micro(CMF), nanofibrils (CNFs), crystalline (CNCs) and amorphous (ANC) nanoparticles. Nanocellulose is a powerful bioadsorbent which combines high resistance with flexibility and a high surface area with flexible surface chemistry. The nanocellulose-generative nanofibers and nanocrystals with adapt-to-surface properties have a broad array of easy hydrolysis and catalyzed pathways. Nanocellulose's superficial function and its capacity to shape

stable sheets mechanically were used to produce water purification membranes. Electrospinning technique is extensively use to fabricate membranes.

The techniques and methods used in maturer polymer membrane areas can provide a better insight into the efficiency in specific industrial applications of nanocellulose-based membranes and measurements against other water purification goods, for example through in-house studies.

The following step of the membrane reseach to nanocellulose water purification is required in association with other nanoparticles to focus on hybrid electrospinning membranes to increase their membrane stability and filtration performance.

4. FABRICATION, CHARACTERIZATION AND APPLICATION OF FLAT SHEET PAN/CNC NANOCOMPOSITE NANOFIBER PRESSURE RETARDED OSMOSIS (PRO) MEMBRANE[4]

Due to the continuous increase in the cost of fossil fuels power generation has drawn lots of attention. Power generation from renewable resources forcing many countries reduced fossil fuel consumption. Companies which have low environmental performance face with strict regulations and high penalties. Because of limited energy efficiency and of solar and wind energy their performance is affected by the wind and solar radiation. In order to find robust technologies continuous research is necessary (Altaee and Sharif, 2015).

Worldwide energy demand mainly based on fossil fuel based technology. Researchers try to find alternative energy sources such as solar, wind, biomass, hydropower, tidal power, ocean thermal energy conversion, etc. because of fossil fuels environmental and political impacts. Many of these technologies promising technologies have geographic limitations or natural intermittence. In addition to alternative sources recently salinity gradient power has the advantage. It is possible to exist naturally occurring salinity gradients all over the world where freshwater meets saline water. Salinity gradients can be harnessed using osmosis. For example, ocean water and river water have about 270 m of hydraulic head chemical potential difference (Ramon et al, 2011).The global potential for power generation is estimated at 1.4-2.6 TW from which approximately 980 GW can be effectively harnessed with an appropriate system design (Ramon et al, 2011; Logan and Elimelech, 2012). Numerous methods have been developed to generate electricity by harnessing salinity gradients such as batteries, supercapacitor flow cells Logan and Elimelech (2012), reverse electrodialysis Logan and Elimelech (2012), Post et al. (2007), osmotic microbial fuel cells and other hybrid technologies (Logan and Elimelech, 2012). Among all

[4] This chapter is based on "Mehmet Emin Pasaoglu and Ismail Koyuncu. Fabrication, Characterization and Application of Flat Sheet PAN/CNC Nanocomposite Nanofiber Pressure Retarded Osmosis (PRO) Membrane. Desalination and Water Treatment (in publication). DOI: 10.5004/dwt.2020.26315

mentioned methods pressure-retarded osmosis (PRO) is one of the most promising (Logan and Elimelech, 2012; Post et al, 2007; Achilli and Childress, 2010; Lee et al, 1981; Gerstandt et al, 2008).

Electrospinning process can be describes as a process in which a high electrostatic field (mainly DC voltage) is applied to form nanofibers with variety of properties. Applying pressure by means of a syringe pump to a polymeric solution or melt, a pendant drop of a polymeric solution at the tip of the capillary tube (spinneret) forms. The tip of the capillary is integrated to an electrode and the other side of the electrode is integrated with a high DC voltage. Electrical forces draw this pendant drop into a hemispherical shape known as a Taylor cone. The viscosity of the polymeric solution is one of the most important parameters forming a stable jet originates from the Taylor cone. When the equilibrium between electrostatic forces and surface tension exists, a Taylor cone is formed. As soon as required electrostatic field applied and surpasses surface tension, an extended Taylor cone is formed and a jet is originated. Polymer jet which is originated from Taylor cone travels linearly for some distance, generally 1-2 cm also known as the jet length. Polymer jet forms a whipping or spiral motion termed as the bending instability. Bending instability cause plastic deformation, which makes fibers very long and thin. Most of the solvent evaporates and finally collected on a grounded collector screen during the jet's flight from the capillary tube (Deitzel et al, 2001).

Cellulose, one of the most important natural polymers, is an unceasing raw material and the main source of sustainable materials on industrial scale. Global quantity of cellulose reaches to 700.000 billion tons, but only 0.1 billion tons of cellulose is currently being used for the production of paper, textiles, pharmaceutical compounds and others. Cellulose, hemicellulose and lignin's are larger units known as elementary fibrils or microfibrils brought together by biomass with about 36 individual cellulose molecules. Elementary fibrils or microfibrils are packed into larger units called microfibrillated cellulose.

The production of cellulosic fibers in nanodimensions have promising properties such as high mechanical performance, hydrophilicity, broad chemical modification, formation of versatile semi crystalline fiber morphologies, large surface area and low density properties, besides renewability and biodegradability. Cellulosic source and the processing conditions dimensions, preparation methods and functions are

changeable. Thus, generally it is possible to categorize nanocellulose into three main groups (Julkapli and Bagheri, 2017).

The production of PRO membranes has progressed more gradually as opposed to FO membranes because of the high pressure added to the draw solution. Many FO membranes can collapse during PRO operations or become severely deformed. The PRO flat-sheet membrane modules need spacers to preserve flow channels and facilitate mass transfer. As well as causing hydraulic pressure losses along the flow channels, the feed spacers eventually deform PRO membranes under high-pressure operations.

In order to increase membrane robustness polymeric membranes is not enough to sustain that much of pressure. It is possible to increase Young's Modules of nanofiber membranes (Pasaoglu et al, 2019). Cellulose has been known for about 150 years, is a renewable and biodegradable polymer, and has for a long time been used as energy source, building material, and clothing. By chemical modification on the cellulose polymers, cellulose derivatives such as cellulose ethers and cellulose ester can be prepared, which have opened up for many novel material and applications for cellulose such as coatings, films, membranes, new building materials, drilling techniques, pharmaceuticals, and food products. In addition, the regeneration process of cellulose has contributed to novel techniques such as spinning of fibers and the viscose process.

The natural fiber strength and stiffness in cellulose fibers comes from the formation of the microfibrils. Microfibrils have a wide range from 2 to 30 nm depending on cellulose source and a length that can be several micrometers. The fibrils are assembled into long threadlike bundles of cellulose molecules stabilized by hydrogen bonds (Helbert et al, 1996; Abe et al, 2007; Börjesson and Westman, 2015).

In this study, research were done on the strengthening and also performance enhancing effects (flux increase as a result of higher hydrophilicity) of the CNC addition on the nanofiber TFC-PRO membrane produced from PAN polymer were investigated. Firstly, pure PAN-based and PAN/CNC doped nanofiber membranes were fabricated. Then, TFC coating was made on the produced membranes and turned into a PRO membrane. In order to find the optimum CNC addition to PAN polymer matrix while forming the most durable PRO membrane, different CNC ratios were prepared. Before, the fabricated membranes were used, their characterizations were made and

performances are compared. Besides, CNC also makes the composite structure more hydrophilic, allowing an increase in net flux.

4.1 Material and Methods

PAN polymer was used to fabricate nanofiber composite membrane from Sigma-Aldrich/USA as nanofiber base material and nanocellulose addition arranged as 1, 2, 5 and 10% wt/wt. DMF used as solvent from AK-KİM Chemicals/Turkey. Tailor made flat sheet electrospinning device was used for fabrication nanofiber membranes over polyester nonwoven support and crystal nanocellulose brought from BGB Company/ Canada.

4.1.1 Fabrication of nanocellulose added support membranes

Dried at 70 ˚C overnight in a vacuum oven, PAN (12 wt %) with a definite dissolved in DMAc by stirring at 30 ˚C for about 48 h. Electrospinning setup (Figure 1) was used to fabricate nanofiber substrate onto a PET non-woven support. The electrospinning conditions were as follows: spinning solution flow rate of 4 ml/min; voltage 30 kV; tip-collector distance, 19 cm; and temperature, 25 ˚C. High voltage is applied to nozzles and polymer solution pressurized by syringe pump.

Five different membranes are made including CNC addition starting from 0, 1, 2, 5 and 10% respectively to PAN polymer.

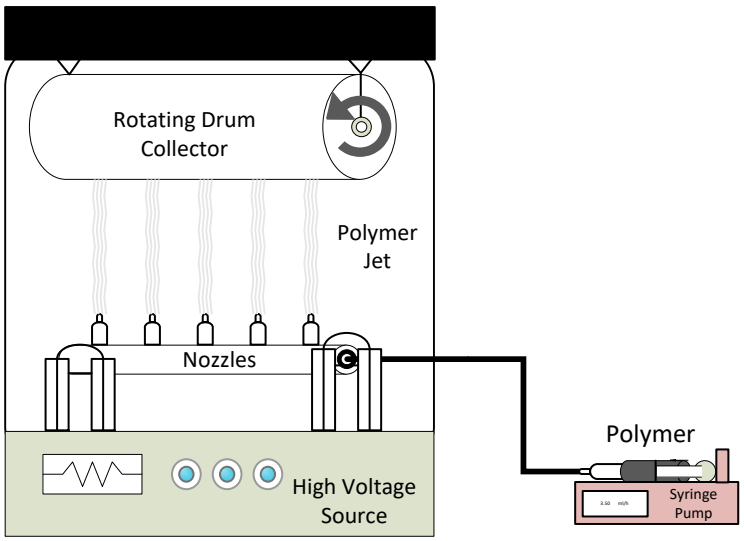


Figure 4.1 : Schematic of electrospinning setup used for nanofiber membrane fabrication.

4.1.2 Fabrication of thin film composite membranes

The membrane substrate was held in distilled water 24 hours for improved wetting before synthesizing the TFC coating. Removal of air bubbles used for processing the MPD (m-Phenylenediamine) solution, 10 minutes with nitrogen gas carried out to remove all the remaining compounds. Once the TMC (1,3,5-Benzenetricarbonyl trichloride) solution bottles were washed, a small amount of hexane was used to wash and extract any residual distilled water and additional TMC applied to hexane during mixing for even distribution and homogeneity.

Formation of an interfacial multi-polymerization layer on top of electrospun substrates between the MPD and TMC is shown in Figure 4.2.

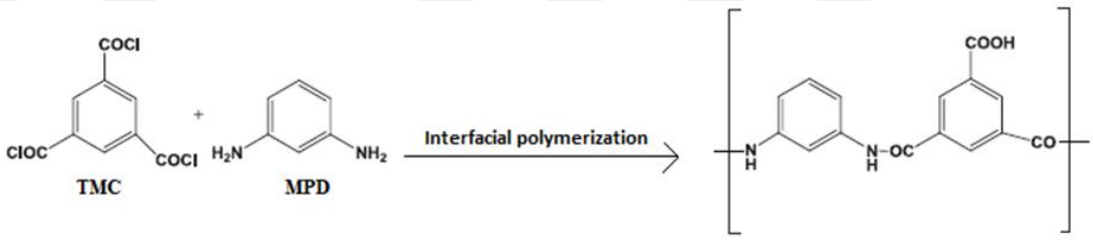


Figure 4.2 : Interfacial polymerization reaction scheme to form the polyamide separation layer (Chia et al, 2020).

Thin film composite membrane coating procedure was given in Table 1.

Table 4.1 : Thin film composite membrane coating procedure.

TMC Concentration	TMC Duration	MPD Concentration	MPD Duration	Air Dry	Oven Dry @ 70 ºC
0.15%	4 min.	3.5%	15 min.	1 min.	5 min.

Fabricated membranes are stored in distilled water after post treatment. A schematic view of the fabrication steps are shown in Figure 3.

4.1.3 Scanning electron microscopy (sem) examination

Advances were made possible in membrane structure analysis by microscopic techniques such as scanning electron microscopy (SEM) (Wyart et al, 2008). SEM is now almost a standard tool for the investigation of surface properties of membranes, including surface topography, alteration of surface by modification, biomacromolecule adsorption, fouling, etc. (Xu et al, 2009).

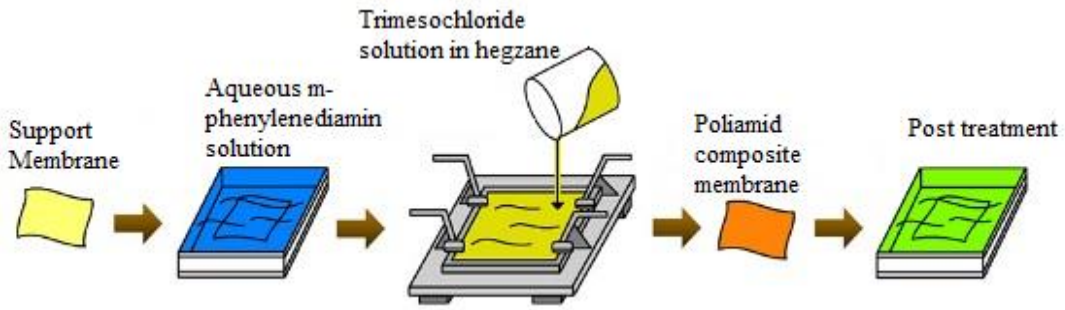


Figure 4.3 : Thin film composite coating procedure.

4.1.4 Pressure retarded osmosis setup

For the experiment, water flow and reverse leakage of salt have been measured. Figure 4 demonstrates the size of the TFC membranes produced from the electrospun-PAN / CNC based PRO system. The membrane cell is divided into rectangular channels with a significant membrane surface area of 0.0058 m2 on both sides of the membrane (length 9 cm, width 6.45 cm and depth 0.3 cm). In order to prevent inconsistencies between the FS and DS sources, 2 O-rings were placed on the outer perimeter of the cell. A medium spacer made of 45 mil (1.14 mm) diamond-type polypropylene screen. The salt concentration changes in both the feed and draw solutions measured by EC meter. Feed side weight changes were recorded with digital balance. As a consequence of water extract from the feed solution side, the initial concentration of drawing solution decreases. PRO tests were performed using 1 M NaCI as draw solution and DI water as the feed solution under standard room temperature. A shematic draw of the PRO test setup is shown in Figure 4.4.

4.2 Results

4.2.1 Scanning electron microscopy (sem) images of the fabricated membranes

Morphological structure of the fabricated nanofiber substrates and thin film composite pressure retarded osmosis membranes were examined with scanning electron microscopy analysis in Figure 4.5 and Figure 4.6 respectively (Quanta FEG 250).

The configuration and the inherent properties of the support layer directly affect the structure and efficiency of the TFC membranes. In general, the "ridge-and-valley" (also referred to as "leaf-like") morphology of the TFC membrane shown in Figure 6 is a well-known feature of interfacial polymerized PA membranes. As already

mentioned, the benefit of microscopic use is that the membrane structure is clearly notified (Lau et al, 2015).

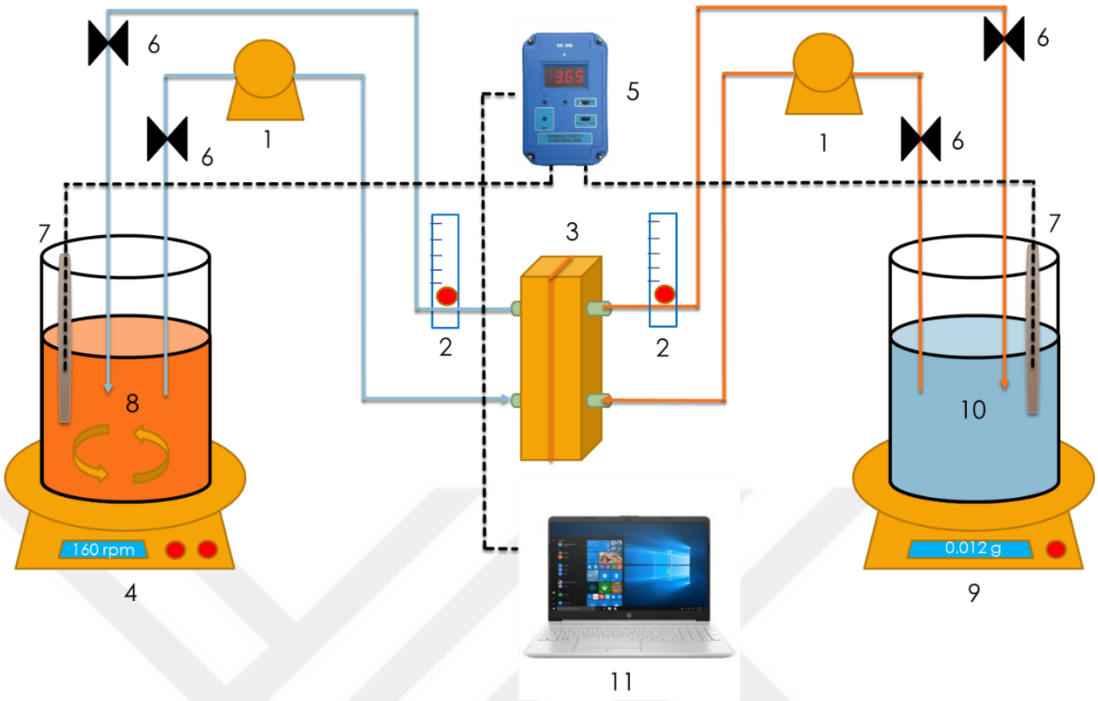
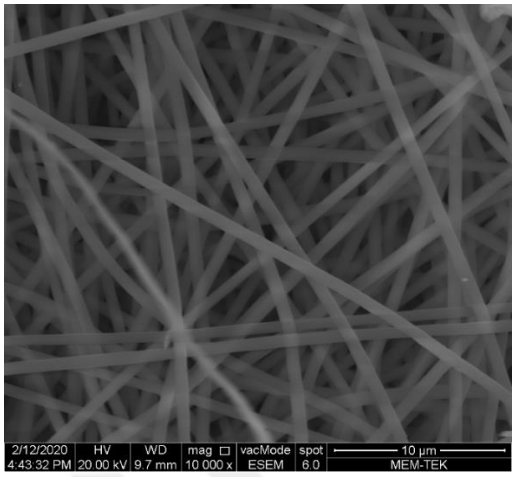


Figure 4.4 : Schematic of PRO setup (1) Circulation pump; (2) Flow meter; (3) PRO membrane and module; (4) Magnetic stirrer; (5) Conductivity meter, (6) Inlet/Outlet valve; (7) Conductivity meter probe; (8) Draw solution tank; (9) Weighing balance; (10) Feed solution tank; (11) Computer.

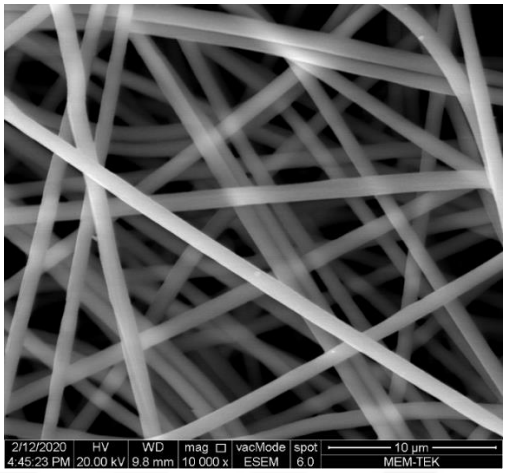
In order to see TFC-PRO membrane structure SEM images were provided in Figure 4.7. The addition of CNC into PAN polymer, it is found that the enhanced hydrophilic nature of PSf substrate upon the addition of hydrophilic could form “nodular” film while the increasing amount of CNC into PAN matrix could result in the formation of some spherical and cylindrical shapes on PA layer.

In general, the most effective TFC RO membranes provide a fairly hydrophobic support for generating thin PA film with strong salt rejection. However, in PRO process and FO process a more hydrophilic support layer is desirable as such supports will have less internal concentration polarization and better water flux. More MPD aqueous solution impregnated in pores in supports of hydrophilic base. In addition, the aqueous MPD solution meniscus was concave in pores after the support containing MPD aqueous solution was dried, and the MPD monomer diffused more slowly out of the pores when contacting TMC solution. The hydrophilic pore wall thus reduced the aggression of the initial MPD "eruption" and resulted in further PA development

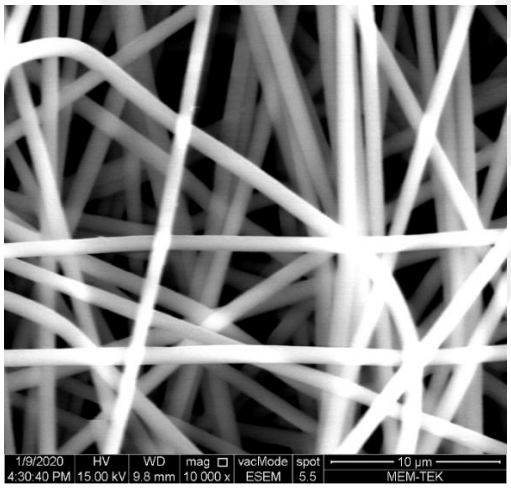
deeper within support layer pores resulting in improved total route duration for water and solute transport (Liu et al, 2019).



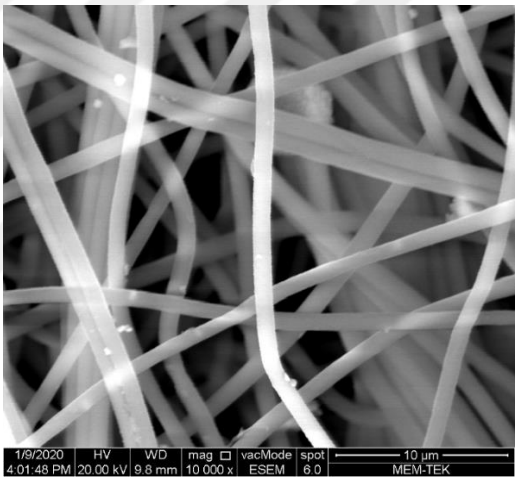
16% PAN 0% CNC



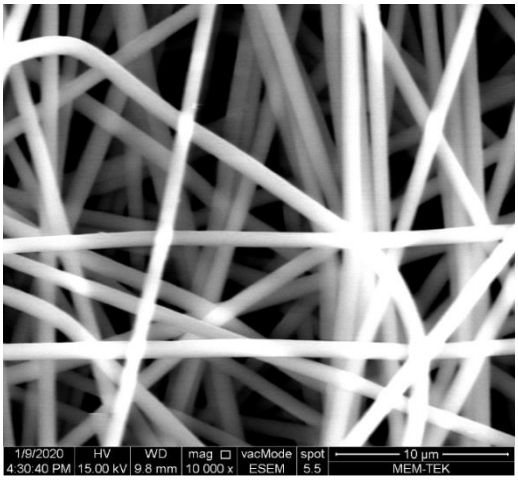
16% PAN 1% CNC



16% PAN 2% CNC



16% PAN 5% CNC



16% PAN 10% CNC

Figure 4.5 : SEM images of fabricated PAN/CNC nanofiber support membranes.

4.2.2 Dynamic mechanical analysis of the fabricated membranes

The mechanical properties of CNC/PAN nanocomposite PRO membranes were determined using Seiko DMA Exstar 6100. Three specimens of each composition were tested at 25 ^{o}C, in accordance with the ASTM D638.

Dynamic mechanical analysis of fabricated membranes is performed for different cellulose nanocrystal addition ratios. In Figure 4.8 results showed that increasing amount of cellulose nanocrystal is increased the young's modules of fabricated membranes which is a vital parameter in order to resist high pressure. The reason of this performance increase is higher viscosity of the polymer solution at higher CNC concentration. The higher the polymer viscosity leads thicker fiber formation. Thicker fibers makes final membrane structure more rigid to higher pressure and environmental conditions.

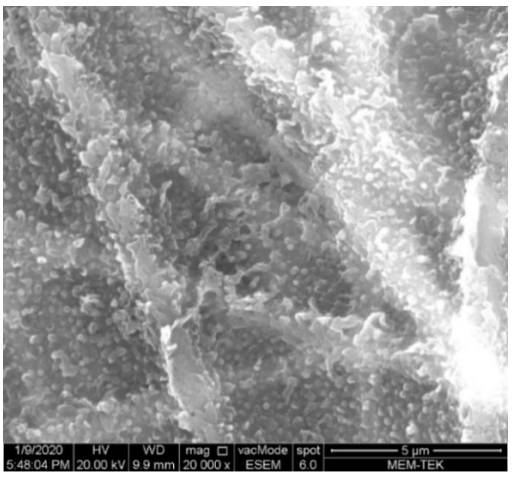
4.2.3 FTIR spectrum of the fabricated membranes

In order to verify the chemical structure of organic molecules and the possible structural changes that occur through CNC addition to the PAN phase, FTIR spectra were reported for the dry support layer membrane. FTIR spectrum was measured using the PerkinElmer Spectrum 100 FTIR Spectrometer (650 to 4000 cm^{-1}) mode of absorption. Figure 4.9 proves that FTIR spectrum of fabricated membranes prove that with the increasing of crystal nanocellulose addition C-N group gave reaction with cellulose group and disappear on 1664.58 cm^{-1} point.

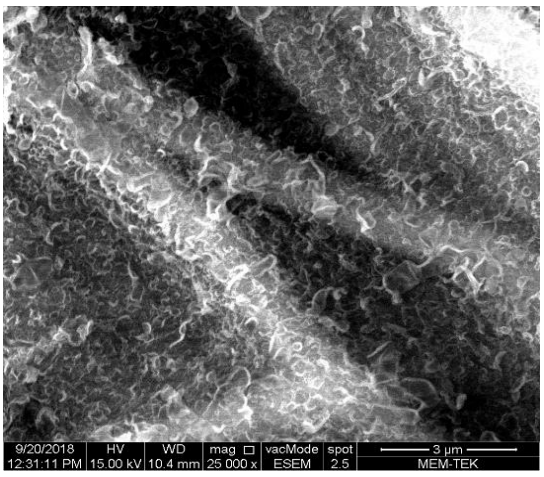
Due to C= O interconnectivity, which is one feature of lignin and lignin/ hemicellulose, the peak of CNC was present at 1620 cm^{-1} in the spectrum (Asrofi et al, 2017). Figure 4.9 also show that PAN spectrum value as 1452 cm^{-1} which is the usual characteristic C-H stretching methylene band and the average vibration of 2923 cm^{-1} is the C-H stretching vibration. The vibration average 2244 cm^{-1} belongs to C≡N (Jin et al, 2018).

4.2.4 Contact angle analysis of the fabricated membranes

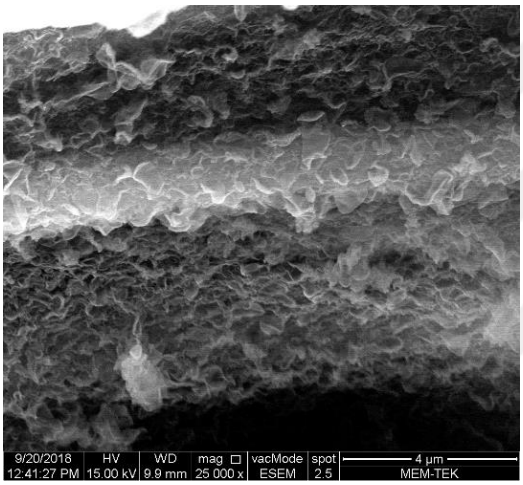
The hydrophilicity of fabricated CNC/PAN nanofiber nanocomposite membranes, 2 μL of DI water drop placed on the membrane surface by contact angle measures using a goniometer (Attension- KSV- Espoo, Finland).



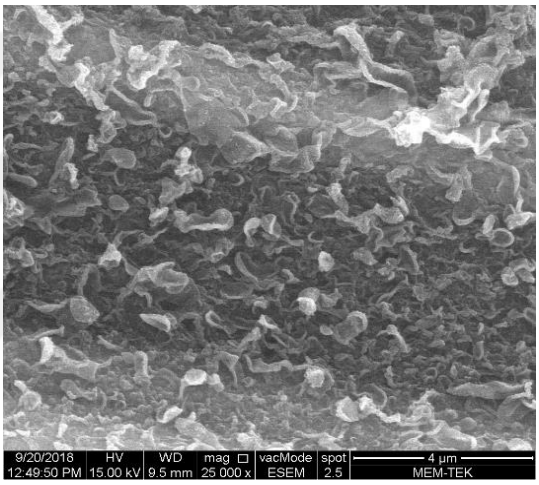
16% PAN 0% CNC



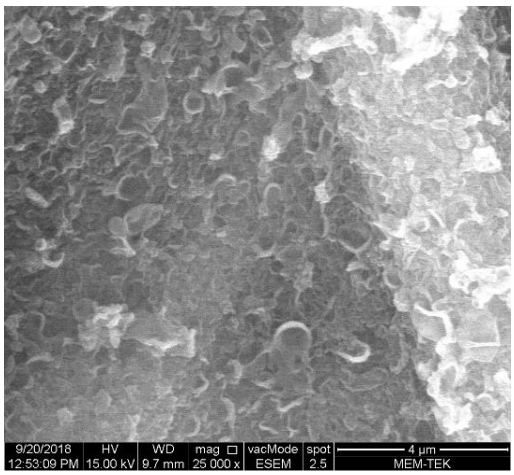
16% PAN 1% CNC



16% PAN 2% CNC



16% PAN 5% CNC



16% PAN 10% CNC

Figure 4.6 : SEM images of fabricated nanofiber TFC-PRO membranes.

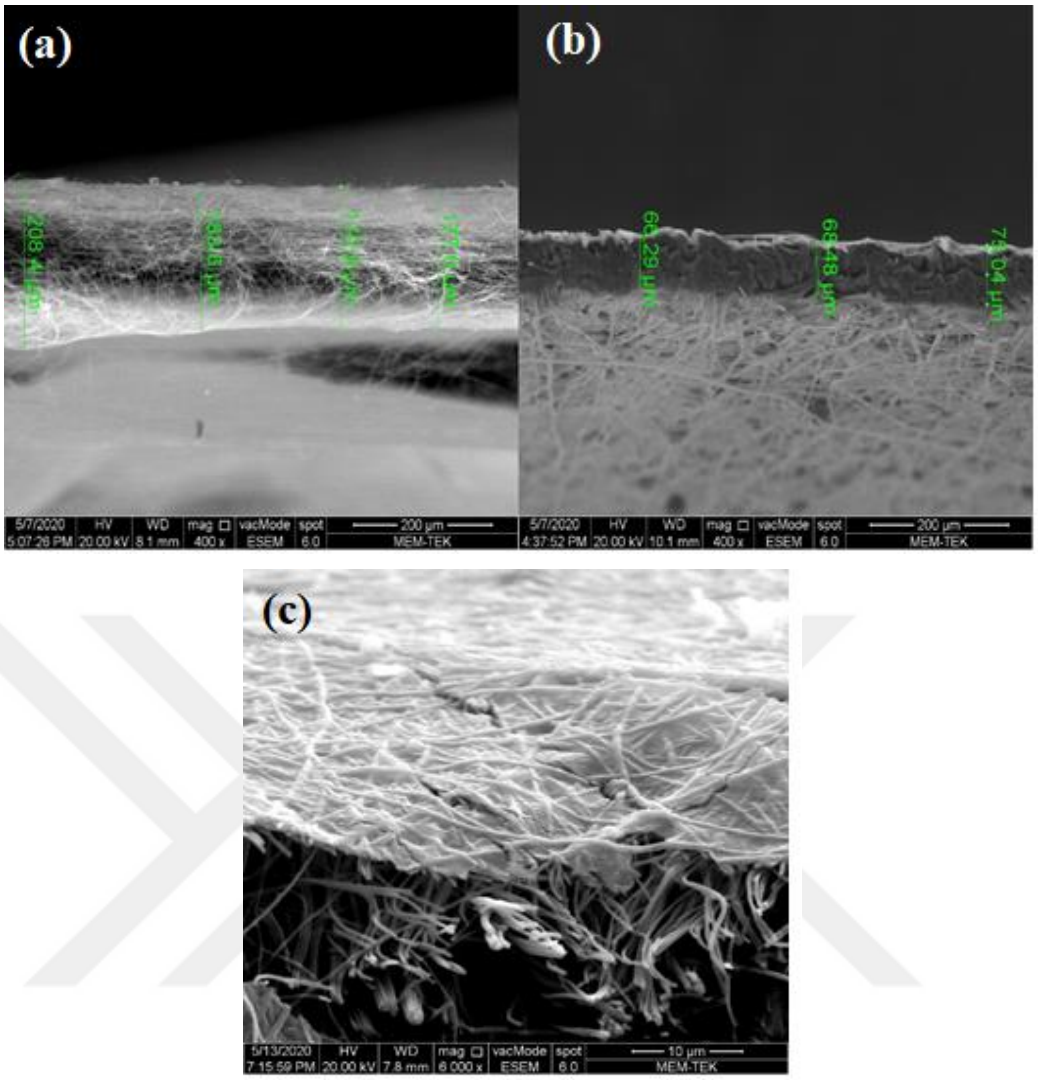


Figure 4.7 : Cross-section SEM images of fabricated nanofiber TFC-PRO membranes (a), PET non-woven support (b) and cross-view of the polyamide coating (c).

From the three different places on each side of the membrane, 10 images are taken and the mean contact angle is averaged. The scale is 0-180^{o} and the difference value is ±0,1 °. The highest and lowest values were discarded, and the mean value was recorded for the eight remaining angles.

According to the results, increasing amount of CNC to PAN polymer solution, contact angle of the fabricated membranes show dramatically decrease which helps to increase membrane water flux in the process that is shown in Figure 4.10. According to the studies in the literature Bai et al. (2017) results shows that increasing amount of CNC helps to decrease membrane contact angle value.

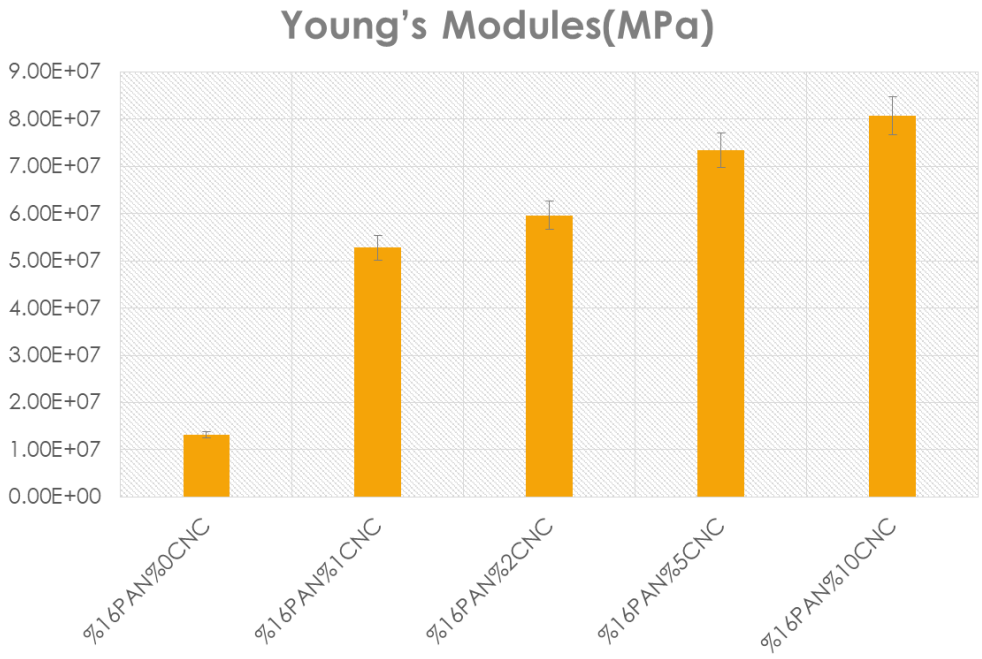


Figure 4.8 : Young's modules of fabricated membranes.

4.2.5 Porometer analysis of the fabricated membranes

Nanofiber membrane porometry is investigated for pore size and distribution. Quantachrome Porofil was used as a weighting agent for porometry measuring with given low surface impedance 16 dynes/cm (Quantachrome Ins., Florida, USA). For porometry measurement, the membranes were classified into 3x3 cm circles and average results are given in Figure 4.11.

Increased polymer molecular weight and viscosity the molecular entanglement of the solution leading to increased fiber diameter (Yousefzadeh, 2017). Concentration of the solution is connected to nanofibers diameter and membrane thickness. The diameter and thickness are in effect related to the distribution of the pore size and the pore form. At very low viscosity of the polymer solution, the electrospinning polymer does not have enough entanglements to establish cohesion, which contributes to the forming of droplets. As a result, breakage happens rather than the production of nanofibers. When the concentration of polymer is above the entanglement concentration required for the entanglement of polymer macromolecular chains, beaded nanofibers are formed (Murthe et al, 2019). Increasing amount of CNC addition into the PAN polymer solution, fabricated nanocomposite nanofiber membranes show decreasing porosity trend. The reason of smaller pore size after 5% CNC addition, fiber diameter is increase and pore size distribution decreases.

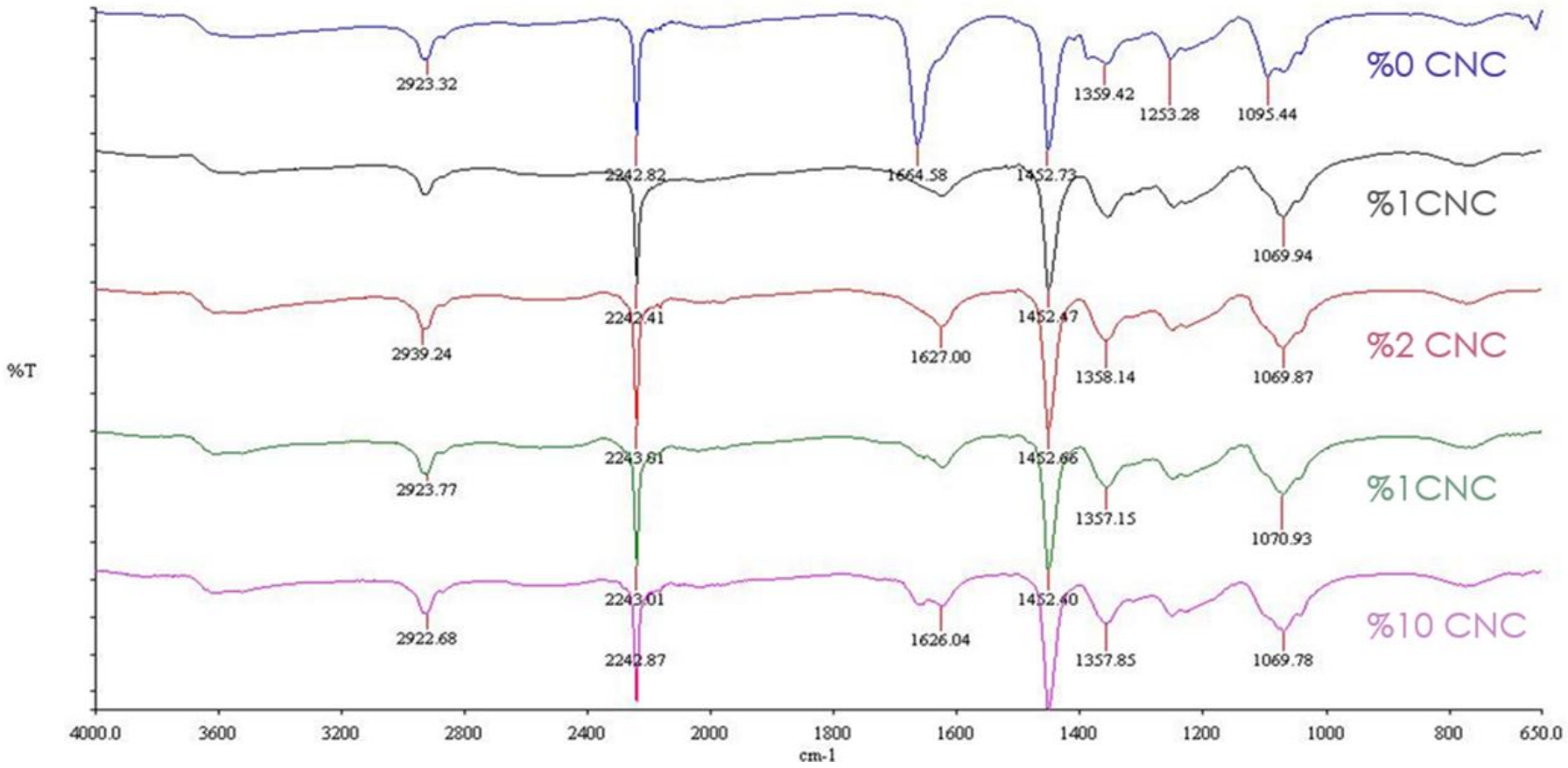


Figure 4.9 : Comparison of FTIR spectrums of fabricated membranes.

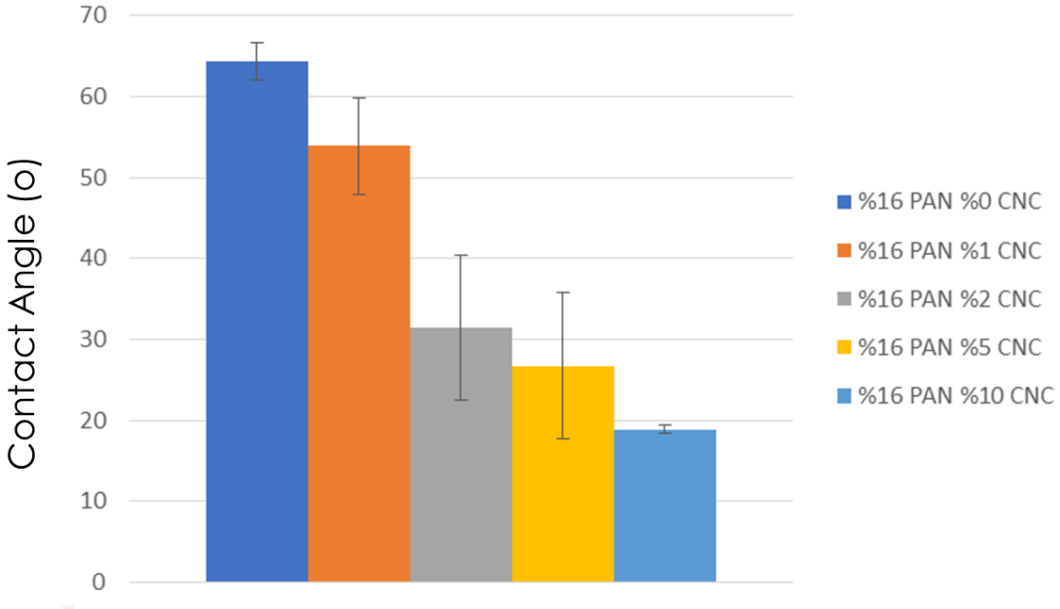


Figure 4.10 : Contact angle of CNC/PAN nanocomposite nanofiber membranes.

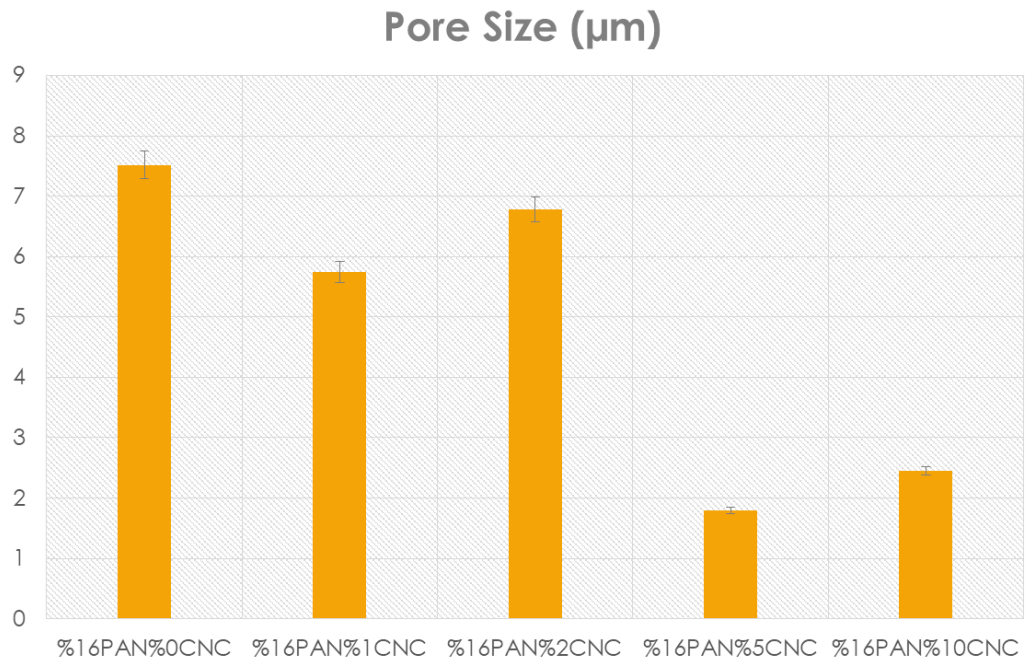


Figure 4.11 : Average pore size measurement of CNC/PAN nanocomposite nanofiber membranes.

4.2.6 Filtration test of the fabricated membranes

Pure water flux test was established in dead-end filtration cells (Sterlitech Corp., Kent, USA). For compaction of the membranes, around 1L of DI water was filter under 0.6 bars.

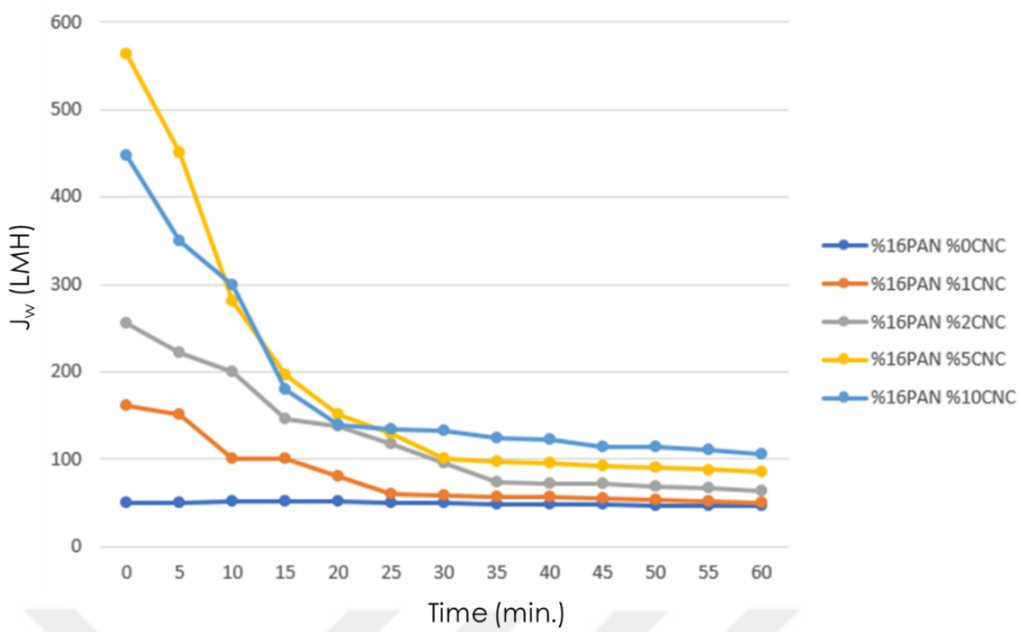


Figure 4.12 : Comparison of PAN/CNC nanocomposite nanofiber membranes pure water flux.

According to the results in the study, increased amount of CNC in PAN polymer matrix increased membrane pure water flux. The main reason of pure water increase with increased CNC content in Figure 4.12 is hydrophilicity. According to a recent study more hydrophilic membranes show higher pure water flux (Bai et al, 2017). So, it can be concluded that, increased CNC content makes PAN/CNC membranes more hydrophilic than pure PAN nanocomposite membranes.

4.2.7 Reverse osmosis separation performance of fabricated pro membranes

All TFC-PRO membranes rejected NaCl at more than 94% when tested at 13.8 bar (200 psi) (Figure 4.13), making them sufficiently selective for PRO applications and energy generation. The average R was 95.0 ± 1.65% for 0% CNC membranes (n=2), 94.4 ± 1.50% for 1% CNC membranes (n=2), 97.0 ± 0.85% for 2% CNC membranes (n=2), 99.0 ± 1.00% for 5% CNC membranes (n = 2), 98 ± 0.90% for 10% CNC membranes (n=2). Each bar represents an average obtained from testing of two separately cast membranes.

4.2.8 Pressure retarded osmosis (pro) test results

The membrane is oriented in the PRO mode, when the draw solution is placed against the active layer and the feed solution against the support layer. This mode is typically used in PRO applications where the draw solution is pressurized and therefore requires

the porous layer's mechanical support on the membrane's feed side. In traditional PRO systems, salinity in the feed water can generate concentrative results of polarization of internal concentration (McCutheon and Elimelech, 2008).

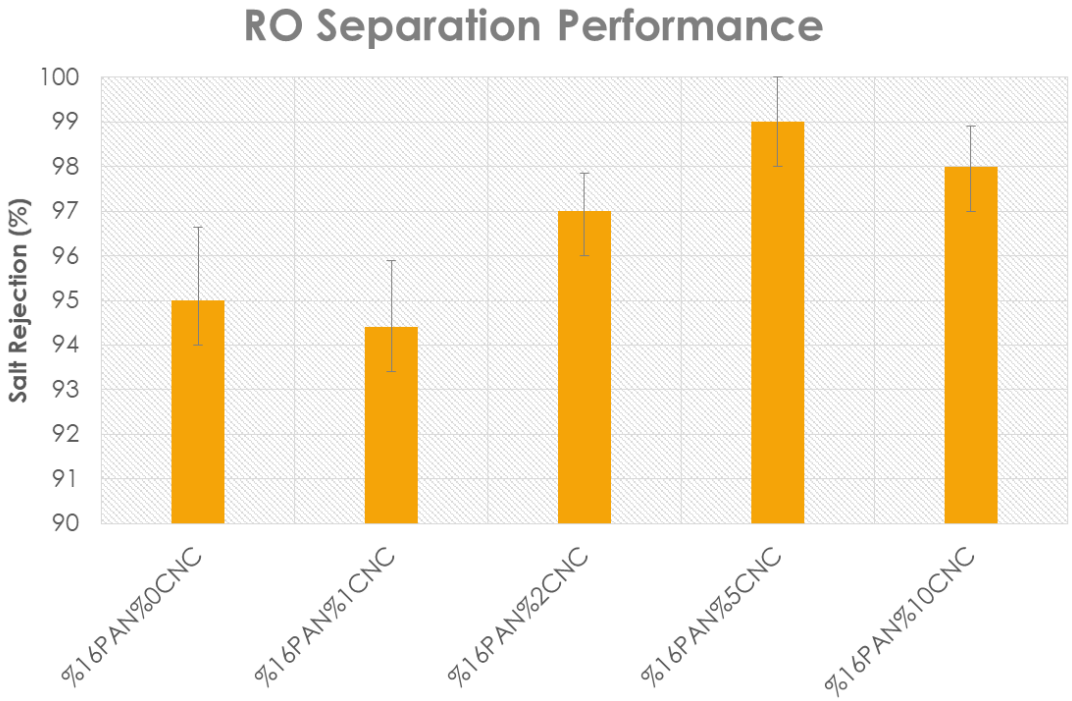


Figure 4.13 : Comparison of PAN/CNC nanocomposite nanofiber membranes salt rejections.

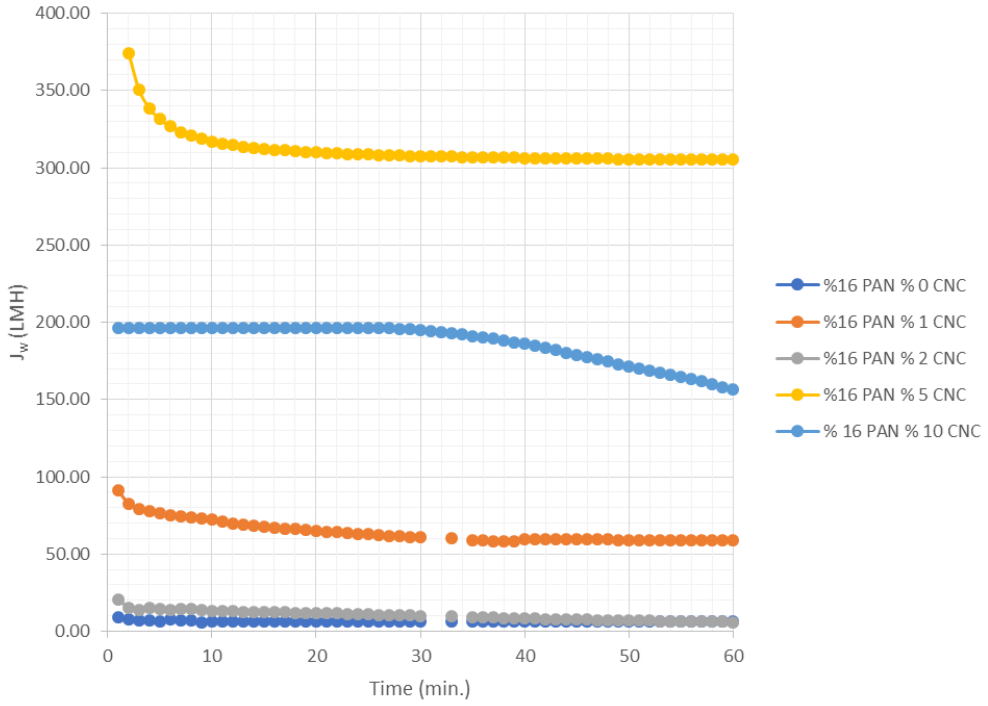


Figure 4.14 : Fabricated PAN/CNC nanocomposite nanofiber TFC PRO membranes water flux (J_W).

Under same conditions %5 CNC added PAN nanocomposite nanofiber TFC PRO membranes performs higher water flux which is shown in Figure 4.14. After 60 minutes of operation, most of the fabricated membranes considerably sustain their original flux.

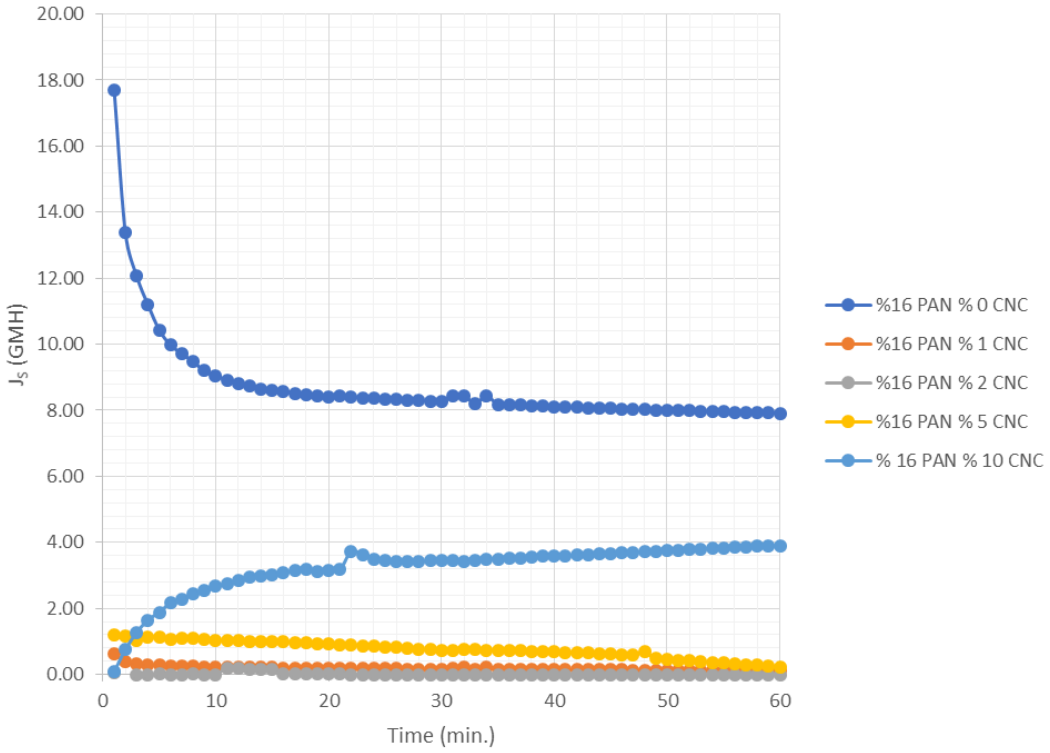


Figure 4.15 : Fabricated PAN/CNC nanocomposite nanofiber TFC PRO membranes reverse salt flux (Js).

Reverse salt flux shows salt leakage from PRO membrane draw solution side to feed solution side. After a quite a while salt leakage dilutes draw side which leads to decrease osmotic pressure difference. So, while ideal PRO membrane manufacturing, it is a must to provide lowest reverse salt flux and higher water flux. In this study, it can be easily seen in Figure 4.15, 5% CNC added PAN nanocomposite nanofiber TFC membranes give best performance.

Another comparison was made between this study and literature in terms of water flux and reverse salt flux of the membranes for PRO application in Table 4.2. The results show that, fabricated membranes in this study have one of the highest Jw/ Js ratio in the literature.

Table 4.2 : Comparisons of PRO performance of various TFC membranes with DI water as feed solutions.

Membrane	Water flux, Jw (PRO) (LMH)	Reverse salt flux, Js (PRO) (gMH)	Js/Jw (g/L)	Jw/ Js (L/g)	Draw Solution	Ref.
PAN/CNC nanocomposite TFC membrane (5% CNC)	300	1.5	0.005	200	1.0M NaCl	This study
FO flat-sheet membrane on sPSU	313	5.3	0.017	58.8	1.0M NaCl	(El Khaldi et al, 2019)
Electrospun-PSf-Based TFC with PET layer-Before Adding SDS	26	$2.26x10^{-3}$	0.00008	0.01150	1.5M NaCI	(Bui et al, 2011)
Electrospun-PSf-Based TFC with PET layer-After Adding SDS	33.6	$4.62x10^{-2}$	0.0013	0.072	1.5M NaCI	
Electrospun-PSf-Based TFC without PET layer-Before Adding SDS	24.0	8.63	0.359	2.78	1.5M NaCI	(Bui et al, 2011)
Electrospun-PSf-Based TFC without PET layer-After Adding SDS	86.1	36.40	0.422	25.32	1.5M NaCI	(Bui et al, 2011)

Table 4.2 (continued) : Comparisons of PRO performance of various TFC membranes with DI water as feed solutions.

Membrane	Water flux, Jw (PRO) (LMH)	Reverse salt flux, Js (PRO) (gMH)	Js/Jw (g/L)	Jw/ Js (L/g)	Draw Solution	Ref.
CTA- ES HTI	8.10	20.03	2.47	0.4	1.0M NaCl	CTA- ES HTI data sheet
TFC-ES HTI	19.31	14.78	0.765	1.3	1.0M NaCl	TFC- ES HTI data sheet
FO flat sheet membrane on cellulose ester substrate	128.8	19.4	0.15	6.67	2.0M NaCl	(Ong et al, 2015)
FO flat sheet membrane on sPPSU (2.5 mole% direct sulfonation) supports	54	8.8	0.163	6.13	2.0M NaCl	(Widjojoa et al, 2013)
FO flat sheet membrane on PES/sPSf supports	47.5	12.4	0.261	3.83	2.0M NaCl	(Wang et al, 2012)

4.3 Conclusions

Fabrication of nanofiber pressure retarded osmosis was performed successfully electrospinning equipment. Fabricated pressure retarded osmosis membranes meet the needs higher pressures during operation. Increasing amount of cellulose nanocrystal (CNC) positively affect the young's modules which makes membrane stronger. FTIR spectrums prove that related groups gave reaction with cellulose group and change the spectrums and it was find out increasing amount of CNC makes membrane more

hydrophilic. Apart from the FTIR spectrum results, it can be concluded that cellulose nanocrystal material is compatible with PAN polymer. Morphology studies performed via SEM equipment were shown that increasing amount of cellulose nanocrystal do not affect dramatically membrane formation until 10% CNC addition. However, in 10%, CNC ratio nanofiber formation was broken and formed beads. Regarding to the PRO performance tests, 5% CNC addition into PAN polymer matrix gives superior water flux and obtains lowest reverse salt flux. Comparison of this study with literature it can be easily seen that PAN/CNC nanocomposite TFC membranes gives maximum water flux and lowest reverse salt flux.

5. TUBULAR PAN/CNC THIN FILM NANOCOMPOSITE (TFN) PRESSURE RETARDED OSMOSIS (PRO) MEMBRANE: FABRICATION AND PRELIMINARY EVALUATION IN DESALINATION PROCESS[5]

5.1 Introduction

Fossil fuels have a variety of harmful environmental effects by the emission of various toxins such as sulfur oxides (SO_x) and nitrogen oxides (NO_x), VOCs and greenhouse gases (Zhu et al, 2010; Alami et al, 2020). Researchers are investigating the potential of generating energy from wind, sun, water, biomass and thermal heat to minimize the use of fossil fuels (Hussain et al, 2017;Tawalbeh et al, 2020; Tawalbeh et al, 2020). Electricity has recently been produced from osmotic pressure using an emerging power generation technology called pressure retarded osmosis (PRO). The mixing of two aqueous solutions of different salinities releases the Gibbs free energy of mixing process, which can be transformed to hydraulic pressure by means of a pressure retarded osmosis (PRO).The electrical power will then be produced by means of hydro-turbines (Tawalbeh et al, 2020; Jia et al, 2014; Skilhagen, 2008).

Pressure retarded osmosis (PRO) has attracted significant interest as a possible technology capable of extracting sustainable osmosis energy from salinity gradients (Cui et al, 2014; Bui and McCutheon, 2014). PRO uses a osmotic pressure difference between feed (FS) and draw solution (DS) pressurized by hydraulic pressure (Loeb, 1976; Yip et al, 2011; Kwon et al, 2021). The energy recovery method relies on placing on the draw stream a higher absolute pressure than that added to the feed stream. As a result, osmosis results in a rise in the flow rate of the high pressure stream – as long as the osmotic pressure differential ($\Delta\pi = \pi_D - \pi_F$) exceeds the difference in the applied absolute pressure ($\Delta P = P_D - P_F$), where π and P are the osmotic and hydraulic pressure of the fluids, and D and F are the draw and feed streams, respectively. This illustrates

[5] This chapter is submitted to Cellulose Journal- Mehmet Emin Pasaoglu and Ismail Koyuncu. " Tubular PAN/CNC Thin Film Nanocomposite (TFN) Pressure Retarded Osmosis (PRO) Membrane: Fabrication and Preliminary Evaluation in Desalination Process"

a classic optimization problem that is essential for the implementation of PRO units, in that higher applied pressure results in higher energy recovery per mole of solvent transfer, but also at a lower rate of solvent transfer at steady state (Manzoor et al., 2020).

The osmotic gradient will determine the quantity of energy generated, similarly as other FO applications. By merging river and seawater, the estimated osmotic energy produced worldwide is between 1750 and 2000 TWh per year, which goes over the limit one-tenth of the world's energy demand with a working pressure of 13.5 bar, equal to a 135 MWC in a hydroelectric power plant (Sikdar, 2014; Chia et al, 2020). The average electricity generation in 2017 is about 481 TWh from biofuels, about 4197 TWh from hydraulics and about 1127 TWh from wind energy, compared to other renewable energy technologies (Tawalbeh et al, 2020; Chia et al, 2020; IEA, 2010).

Many of the studies published in the literature is aimed at improving the viability of using PRO for generating electricity, although on small-sized systems. Figure 5.1 shows recent PRO research focus directions. In order to prove its feasibility in extraction of energy back in 1976 using hollow fiber membranes, Loeb et al. (1976) are experimentally testing the PRO technique. Mehta and Loeb (1978) examined the influence of osmotic pressure on high pressures. Water transport was modeled in the PRO method in 1981. In this model, the internal effects of concentration polarization were considered (Lee et al, 1981). In 1990, Loeb and his collaborators perfomed an analysis evaluating the mechanical efficiency of the continuous operation of the PRO plant. The continuous operation of the underground PRO plant and the alternating flow configuration of the terrestrial PRO plant (Loeb et al, 1990). In 2009, the Norwegian company (Statkraft) built Loeb's first design of the PRO plant in Oslo, Norway (Statkraft, 2009). The prototype of Statkraft is situated approximately 60 km south of Oslo, where the capital of Norway. Because of the expensive pre-treatment of river water needed and the limited capacity of electricity due to the small osmotic differential pressure between the seawater and the river, work at Statkraft terminated in December 2013 (Sarp et al, 2015). The internal concentration polarization model was developed by Xu et al. (2010) to integrate the effect of drawing solution using spiral wound FO membrane modules. Increasing water permeation across the membrane has been shown to raise the concentration of draw solution; nevertheless, the negative impact of internal polarization of concentration has also been enhanced

(Xu et al, 2010). Much of the studies performed up to 2011 centered on the investigation and enhancement of membranes in PRO operations. It should be mentioned that a thin film consisting of an active layer of polyamide and a support layer of polysulfone for the PRO process was developed by Yip et al. (2011) to enhance their hydrophilic properties and improve water permeability, polydopamine was applied over the supporting layers of two suitable RO membranes (Arena et al, 2011).

Despite promising developments in PRO technology, owing to a lack of membranes with suitable high power density and acceptable durability under highly pressurized PRO operating conditions, the PRO process has yet to be commercialized (Skilhagen et al, 2008; Cai et al, 2016). For instance, because of their poor water flow and low power density, prototype commercial cellulose acetate (CTA) membranes have not been shown to be commercially viable for use in PRO (under the conditions of smaller than 1 W m^{-2} using river water as feed and seawater as draw solution) (Kwon et al, 2021, Song et al, 2013; Chou et al, 2012; Vos, 1966).

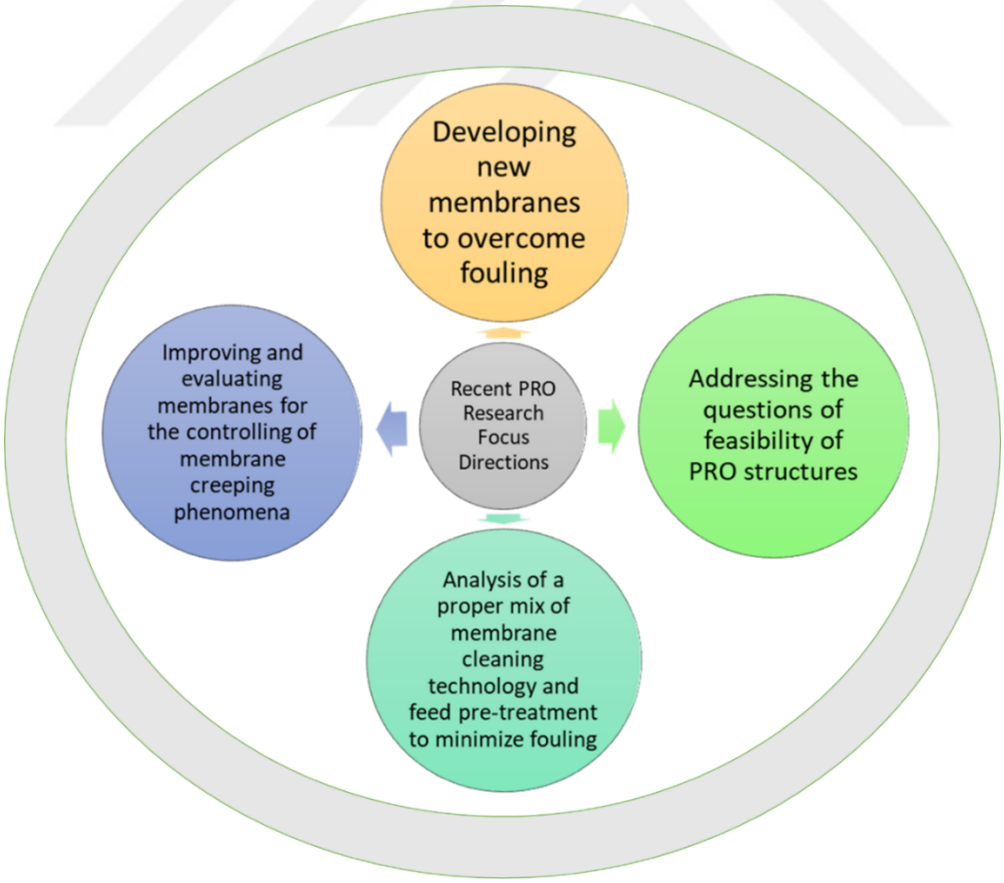


Figure 5.1 : Recent PRO research focus directions (Redrawn from Tawalbeh et al, 2020).

Apart from the recent PRO research tendency we focused on the strengthening the membrane material cope with creeping phenomena in this study. One of the most important purposes is to use less petro-chemical materials during the production of membranes, while increasing the strength in the use of the membrane in the PRO process.

We concentrate on the biocompatible approach in this study by adding cellulose nanocrystals (CNCs) to the TFC membranes based on nanofiber. Natural needle-rod fragments arising from acid hydrolysis of raw cellulose are CNCs, also known as nanocrystalline cellulose (NCC) (De Souza Lima, 2004). The amorphous segments of cellulose, consisting of cellulose fibres, lignin, waxes, etc., degrade and remain extremely crystalline as biomass is processed in a harsh acid environment (Asempour et al, 2018). Cellulose can be defined as a high molecular weight homopolymer of β-1,4-linked anhydro-D-glucose units, irrespective of their source, in which each unit is 180° corkscrew relative to its neighbors and the repeat section is commonly used as a glucose dimer known as cellobiose (Figure 5.2). With respect to the termini of its molecular axis, each cellulose chain has dimensional chemical asymmetry: one end is a group that is chemically reduced (i.e. hemiacetal unit) and the other end is a pendant hydroxyl unit, the nominal non-reducing end. The number of glucose units or the degree of polymerization (DP) is up to 20 000, but shorter cellulose chains may occur and are often located in the primary walls of the cells (Habibi, 2010).

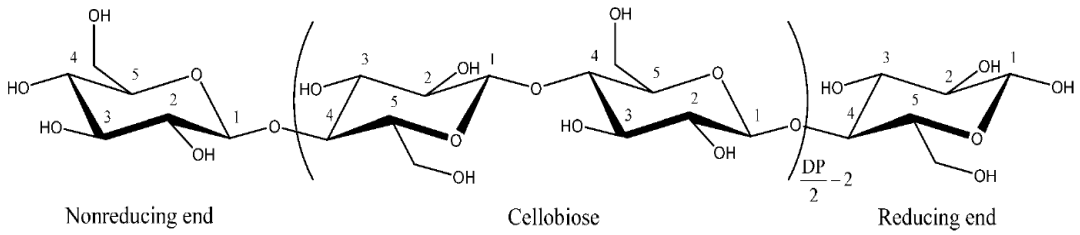


Figure 5.2 : Chemical composition of cellulose (Habibi et al, 2010).

Depending on the source of cellulose and the conditions of acid treatment, the size of the CNCs varies, but typically they are a few hundred nanometers long and a few nanometers in diameter (Habibi et al, 2010; Peng et al, 2011). They have a high specific density, a large specific surface area and a large negative zeta potential, as well as Young's modulus. They also have a highly reactive surface that makes them favorable for chemical functionalization due to the presence of the single bond -OH

groups (Habibi et al, 2010; Peng et al, 2011). CNCs are biodegradable, renewable, have very low impacts on the ecosystem and are generally referred to as non-toxic and harmless particles (Habibi et al, 2010; Peng et al, 2011; Canada 2020; Kovacs et al, 2010; Roman et al, 2009; Hanif et al, 2014; Mahmoud et al, 2010; Bai et al, 2012; Li et al, 2011; Daraei et al, 2017. For a wide variety of possible uses, these appealing properties of CNCs have attracted considerable interest in PRO membrane fabrication.

Usually, two categories of membranes have been used extensively for PRO membranes. First one is the thin-film composite (TFC) membrane with selective layers on porous supports and the second one is an engineered shelled membrane developed using cellulose acetate (CA) and cellulose triacetate (CTA) (Sun and Chung et al, 2013; Lee et al, 2020). It is feasible to fabricate TFC membranes to ensure support, and selective layers have a greater flux of water than CA or CTA membranes (Gonzales et al, 2019). PRO membranes using a TFC membrane have also been studied in several researches (Lee et al, 2020) . In other experiments, Bui and McCutcheon, (2014) and Song et al. (2013) developed nanofiber-based PRO membranes with nanofiber support for polyacrylonitrile (PAN). Nanofibers are known to have a high potential for use in the development of osmotically-driven membranes due to their high porosity and low tortuosity (Bui et al, 2014; Shirazi et al, 2017; Son et al, 2018). In fact, the produced membranes achieved a power density of 21.3 W/m^2 @ 15.2 bar and 8.0 W/m^2 @ 11.5 bar, when 1.06 M NaCl and 0.5 M NaCl were used as drawing solutions, respectively (Lee et al, 2020).

Mentioned studies have proved the feasibility of nanofibers for use in the production of PRO membranes with high power density. However, owing to their comparatively lower mechanical flexibility, at high hydraulic pressures in nanofiber oriented PRO membranes, the risk of membrane deformation still exists. In order to address the poor mechanical stability of nanofiber-based PRO membranes at different ratios, the mechanical stability of polyacrylonitrile (PAN) nanofiber support was enhanced by CNC composites and the nanofiber structure was controlled.

5.2 Experimental

5.2.1 Materials

Polyacrylonitrile (PAN) homopolymer (Mw=150000 Da from Sigma-Aldrich/USA) nanofiber base material and nanocellulose addition arranged as 1, 2, 5 and 10% wt/wt. DMAc used as solvent from AK-KIM Chemicals/Turkey. Tailor made tubular electrospinning device was used for fabrication nanofiber membranes over hollow braided rope and crystal nanocellulose (CNC) brought from BGB Company/Canada and hollow braided rope from Kord Technical Ropes/Turkey.

5.2.2 Fabrication of nanofibrous tubular mats on hollow braided rope

The configuration of the multi-nozzle bottom-up electrospinning system used in this research is shown in Fig. 5.3. A voltage adjuster between the range of 0-40 kV was used to change the voltage. The distance between the nozzle and the collector was also manually controlled to achieve a uniform fiber formation and fiber layers without any beads. In addition, a heat treatment system was used at a specified temperature and time on tubular nanofiber membranes. The PAN polymer with 16% DMAc solvent was dissolved by overnight stirring. For each condition, the spinning shaft speed was kept constant. The solution mixture was filled into a syringe and injected at a defined flow rate into the nozzle system. A hollow braided rope mounted on thin cylindrical steel attached to the spinning rod was coated with nanofibers. Each production step is shown in Figure 5.3.

5.2.3 Fabrication of thin film nanocomposite (tfn) tubular cnc pressure retarded osmosis membranes

Fabricated support nanofiber membranes are primarily immersed in purified water for at least one hour. Aqueous m-phenylenediamine (MPD) solution and trimesochloride (TMC) solution are then applied in hexane. In order to remove air bubbles nitrogen gas applied to the MPD solution. Interfacial polymerization reaction scheme is shown in Figure 5.4. Fabricated membranes are preserved in distilled water after post-treatment. A schematic view of the manufacturing steps as shown in Figure 5.5.

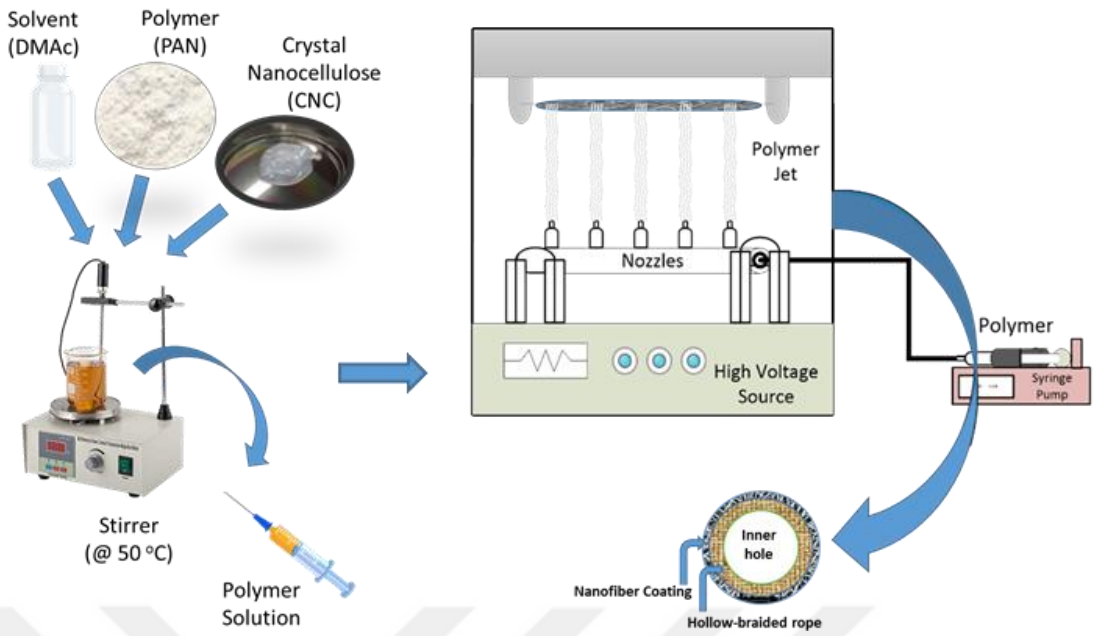


Figure 5.3 : Fabrication steps of nanofibrous tubular mats on hollow braided rope.

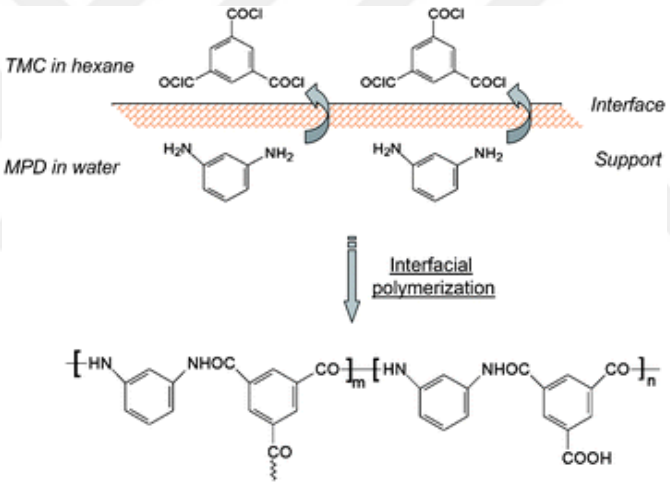


Figure 5.4 : Interfacial polymerization reaction mechanism to form polyamide (PA) separation layer (Li and Wang, 2010).

Thin film nanocomposite membrane coatig procedure is given in Table 5.1.

Table 5.1 : Thin film nanocomposite membrane coating procedure.

MPD Concentration	MPD Duration	Air Dry	TMC Concentration	TMC Duration	Oven Dry @ 70 °C
3.5%	15 min.	1 min.	0.15%	4 min.	5 min.

5.2.4 Pressure retarded osmosis setup

For the experiment, water flow and reverse leakage of salt have been measured. Figure 5.6 demonstrates the size of the TFC membranes produced from the electrospun-PAN / CNC based PRO system. Pneumatic PE hose with an internal diameter of 6 mm was used as a housing in cross-flow experiments. The holes at both ends of the hose is filled with heavy duty industry scale silicone. The concentrate was circulated via the shell-side of the membrane, while the feed solution was contacted through the lumen-side.

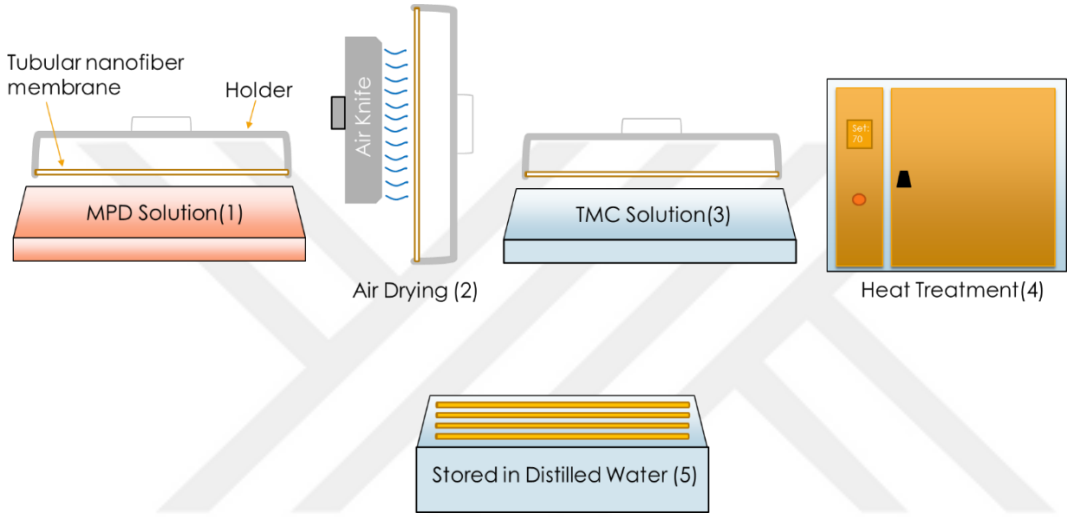


Figure 5.5 : Fabrication steps of nanocomposite (TFN) tubular cnc pressure retarded osmosis membranes.

The salt concentration changes in both the feed and draw solutions measured by EC meter. Feed side weight changes were recorded with digital balance. As a consequence of water extract from the feed solution side, the initial concentration of drawing solution decreases. PRO tests were performed using 1 M NaCI as draw and distilled water as the feed solution under standard room temperature. Fabricated membrane modules are shown in Figure 5.6. Membrane modules have been developed to facilitate the study of water and salt fluxes in cross-flow system. A shematic draw of the PRO test setup is shown in Figure 5.7.

Figure 5.6 : Fabricated PAN/CNC TFN PRO membrane modules.

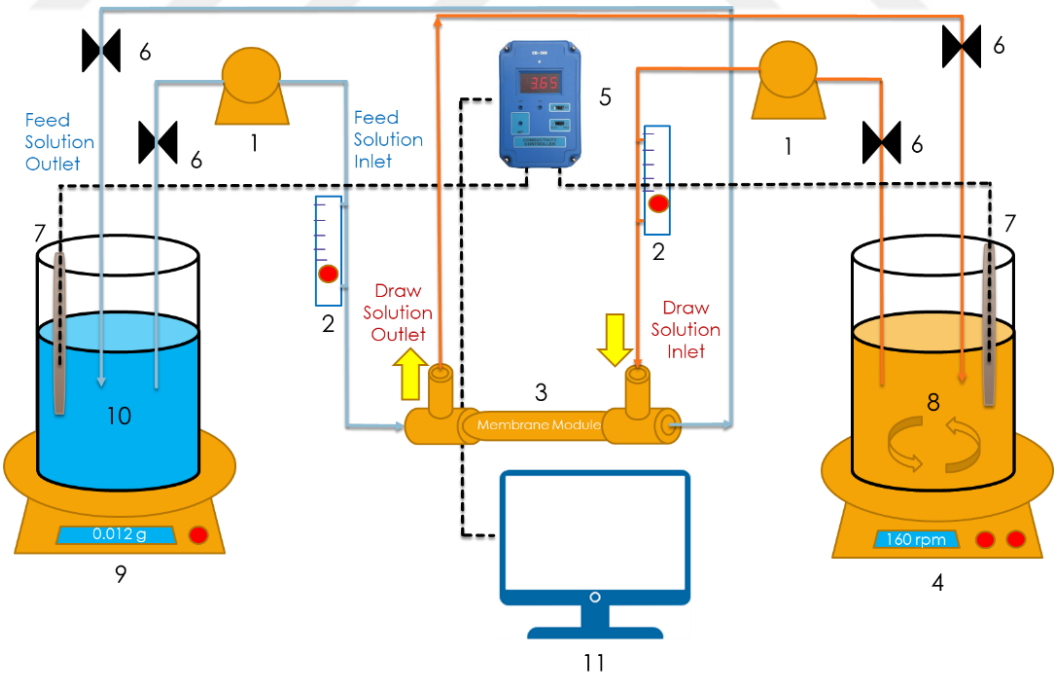


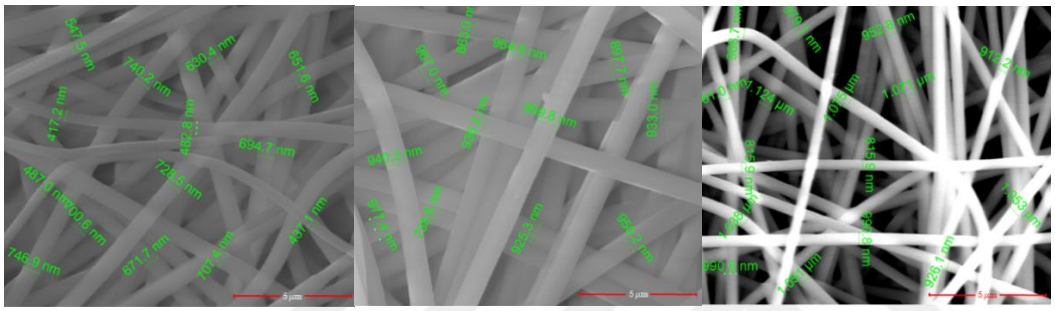
Figure 5.7 : Schematic of PRO setup (1) Circulation pump; (2) Flow meter; (3) PRO membrane module; (4) Magnetic stirrer; (5) Conductivity meter; (6) Inlet/Outlet valve; (7) Conductivity meter probe; (8) Draw solution tank; (9) Weighing balance; (10) Feed solution tank; (11) Computer.

5.3 Results and Discussion

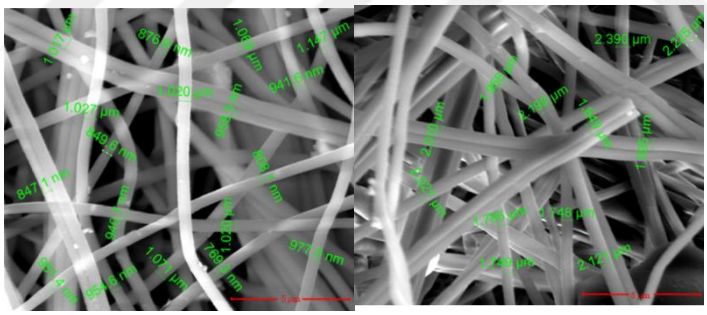
5.3.1 Characterization of tubular nanofibrous membrane

5.3.1.1 SEM analysis of nanofibrous support and thin film nanocomposite (tfn) layer

The morphology of nanofiber membranes and thin film nanocomposite (TFN) layer were described by the FEI Quanta FEG 250/Czech Republic equipment. Nanofiber membranes coated with Gold and Palladium (Au-Pd) with a thickness of nearly 3-4 nm using Quorum SC7620 equipment.



a) 16%PAN 0%CNC b) 16%PAN 1%CNC c) 16%PAN 2%CNC

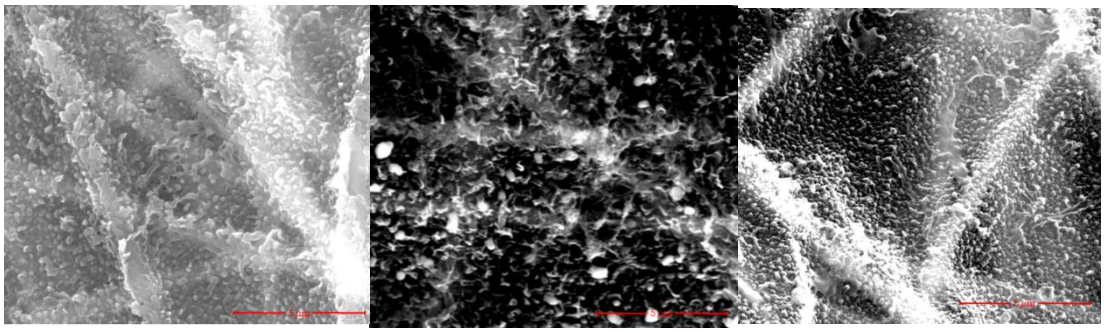


d) 16%PAN 5%CNC e) 16%PAN 10%CNC

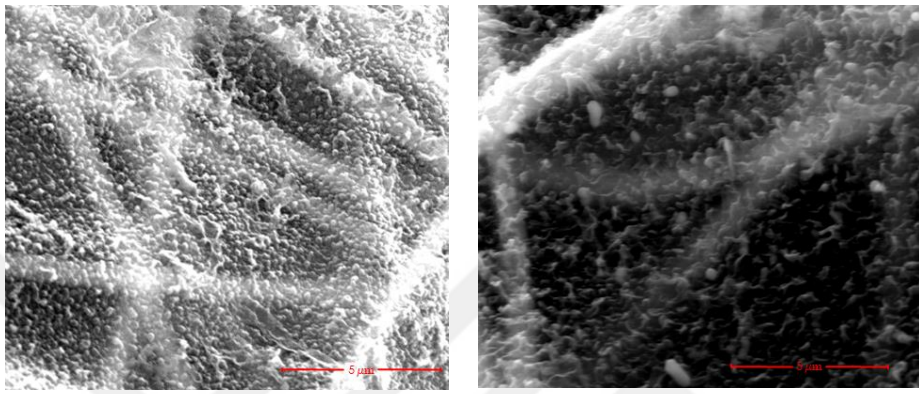
Figure 5.8 : Surface SEM images of tubular nanofibrous support.

5.3.1.2 Determination of pore size

Using the Quantachrome 3G Porometer, the pore sizes were measured.For porometry measurements, the membranes were split and pinced on both ends. On the basis of the total area, the pore sizes were calculated. Quantachrome Porofil was used as a porometry weighting agent with a low surface impedance of 16 dynes/cm (Quantachrome Ins., Florida , USA).



a) 16%PAN 0%CNC b) 16%PAN 1%CNC c) 16%PAN 2%CNC



d) 16%PAN 5%CNC e) 16%PAN 10%CNC

Figure 5.9 : Surface SEM images of thin film nanocomposite (TFN) layer.

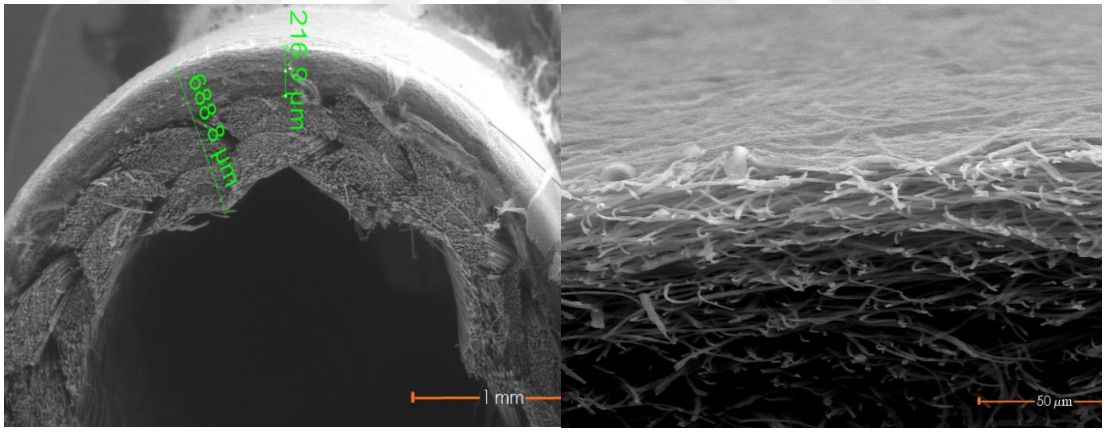


Figure 5.10 : Cross section SEM images of thin film nanocomposite (TFN) layer.

It is commonly recognized that decreasing the concentration of the solvent or the molecular weight can decrease the fiber diameter due to lower viscosity (Tan et al, 2005). The viscosity of the solution produces an anti-electrostatic repulsion force responsible for the stretching and thinning of the solution jet. Unlike several other parameters, it has repeatedly been shown that higher viscosity results in higher fiber diameters, irrespective of the material used.

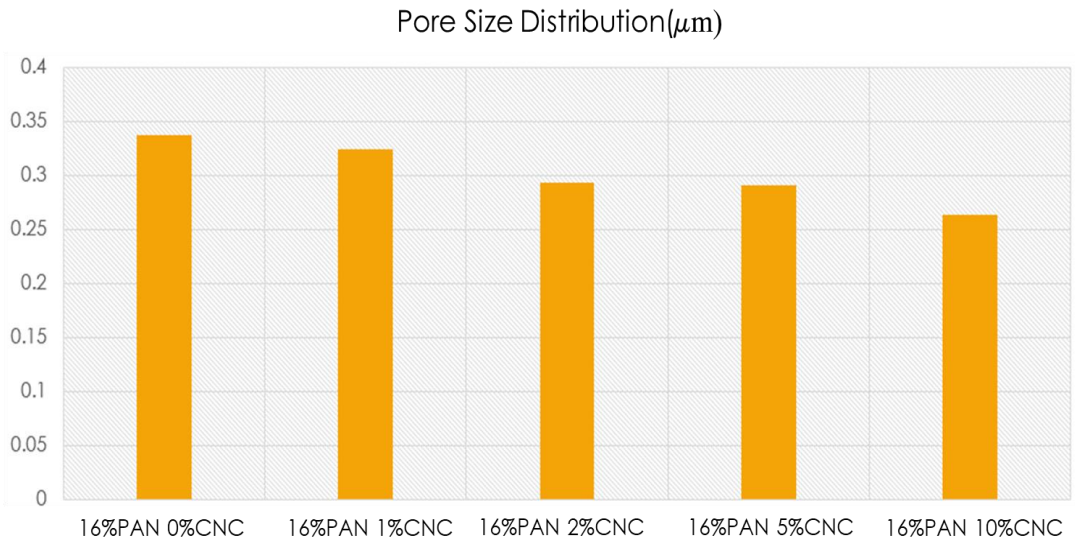


Figure 5.11 : Average pore size distribution measurement of CNC/PAN nanocomposite nanofibrous membranes.

In effect, the diameter and thickness relate to the distribution of the pore size and the shape of the pore. The electrospinning polymer does not have adequate entanglements to create stability at a very low viscosity of the polymer solution, which leads to droplet formation (Murthe et al, 2019). In Figure 5.11, it reveals that increased volume of CNC addition to the PAN polymer solution, fabricated nano-composite nanofiber membranes display a diminishing porosity pattern (Pasaoglu and Koyuncu, in press).

5.3.1.3 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of fabricated membranes are performed for different CNC additon ratios using SEIKO Dynamic mechanical spectrometer Extar 6100/Japan. DMA can be used for research into the viscoelastic behavior of the nanofibrous membranes specimens. The DMA is capable of applying a given oscillatory force to a test specimen, and the strain or displacement is subsequently evaluated.

Before testing, the produced membranes were taken by stripping from the tubular hollow braided rope and the measurements were made in the test equipment similar as the measurement of flat-sheet nanofiber membranes. Figure 5.12 shows that an increasing amount of CNC is being increased for youngs' modulus of engineered membranes, which is a critical parameter for resistance to high pressure. The higher viscosity of the polymer solution at higher CNC is the factor for this efficiency improvement.

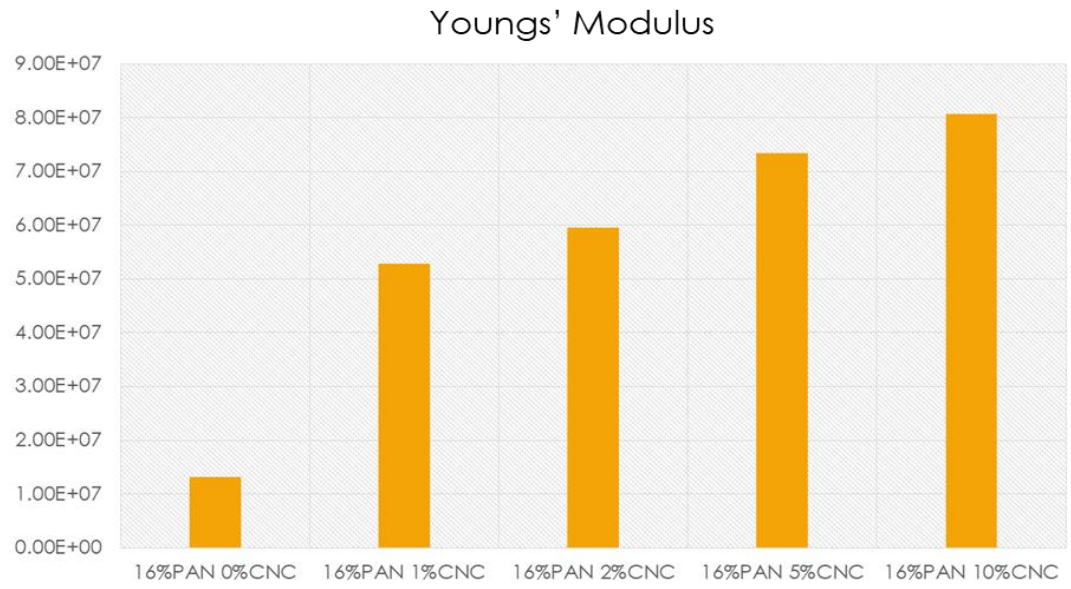


Figure 5.12 : Youngs' modulus of fabricated membranes.

5.3.1.4 Fourirer-transform infrared spectroscopy (FTIR) of the fabricated membranes

Fourier-transform infrared spectroscopy (FTIR) has been identified for the dry support layer membrane in order to check the chemical composition of the organic molecules and the potential structural modifications that occur by CNC in addition to the PAN process.

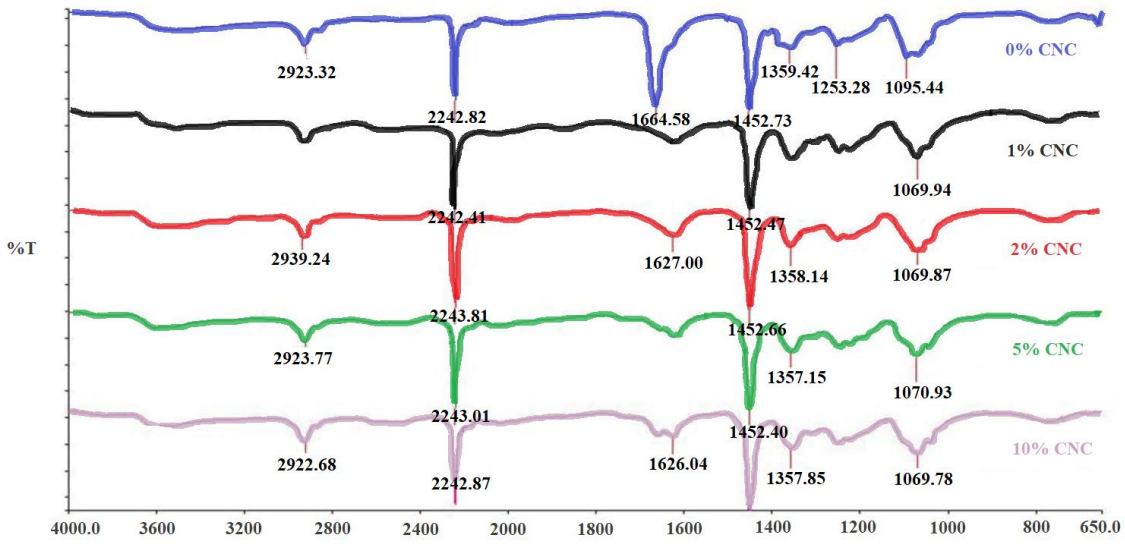


Figure 5.13 : Comparison of FTIR spectra of fabricated membranes.

The FTIR spectrum was measured using the Perkin Elmer Spectrum 100 FTIR Spectrometer/USA (650–4,000 cm–1) absorption mode. Figure 5.13 reveals that the FTIR range of fabricated membranes proves that with a rise in crystal nanocellulose,

the C–N group reacted with the cellulose group and disappeared at 1,664.58 cm–1 point.

The peak of CNC was present at 1,620 cm-1 in the spectrum due to C = O interconnectivity, which is one characteristic of lignin and lignin / hemicellulose [49]. Figure 5.13 also indicates that the PAN spectrum value of 1,452 cm-1 is the normal C-H stretching methylene band characteristic, and the C-H stretching vibration is the typical vibration of 2,923 cm-1 (Jin et al, 2018).

5.3.1.5 Contact angle analysis of the fabricated membranes

The hydrophilicity of fabricated CNC/PAN nanocomposite membranes are measured using a goniometer (Attension-KSV-Espoo/Finland) with 2 µL of DI water droplet. 10 images are obtained from three different points on different sides of the membrane, and the mean average contact angle is recorded. The range is 0°-180° and the magnitude of the difference is ± 0.1°. According to the findings, the contact angle of the fabricated membranes indicates a dramatic decrease in the growing amount of CNC to PAN polymer solution, which tends to increase membrane water flux in the process shown in Figure 5.14. According to literature studies Voisin et al. (2017), Cheng et al. (2017), Bai et al, (2017) the increasing amount of CNC helps reduce the value of the membrane contact angle.

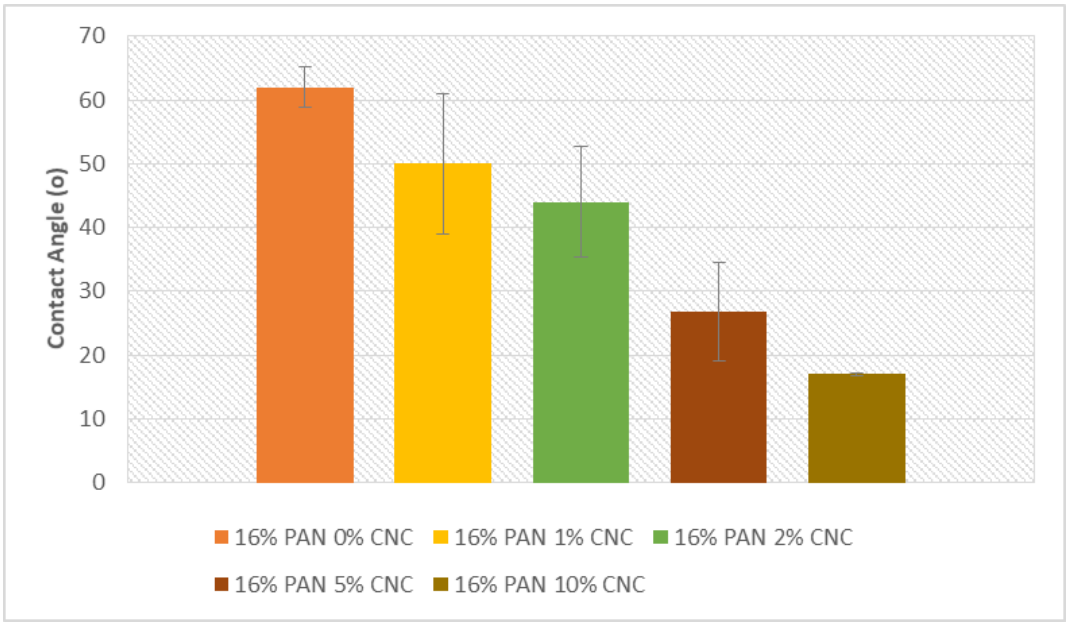


Figure 5.14 : Contact angle comparison of CNC/PAN TFN nanofiber membranes.

5.4 Pro test results

The membrane is PRO-oriented while the drawing solution is placed against the active layer and the feed solution is positioned against the support layer.Under the same conditions, 2% CNC added PAN nanocomposite nanofiber TFC-PRO membranes perform higher water flux which is shown in Fig. 5.15.

The addition of CNC in PAN polymer solution obviously allowed the flux increase in the membranes. Although a very high flux was seen on the membrane with 5% CNC additive, this flux value decreased rapidly. After 60 minutes of operation, most of the fabricated membranes considerably sustain their original flux.

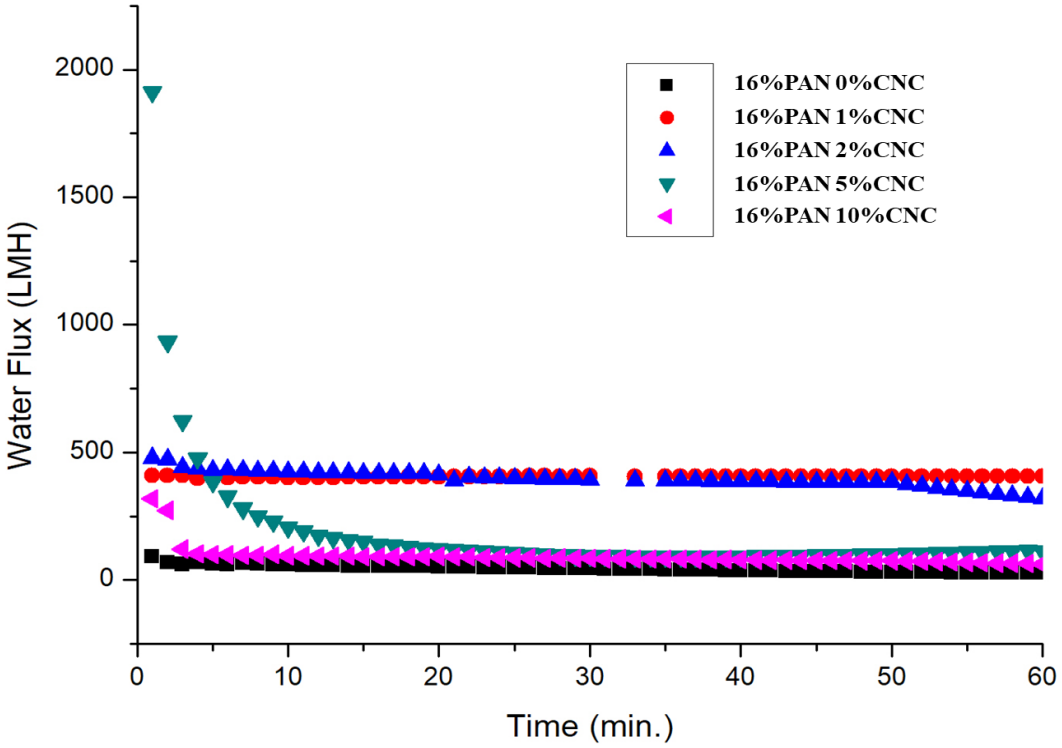


Figure 5.15 : Fabricated PAN/CNC nanocomposite PRO membranes water flux (Jw).

Reverse salt flux indicates salt leakage from the PRO membrane to the side of the feed solution. For such a while of salt leakage, the draw side is diluted, leading to a reduced osmotic pressure difference. Thus, although ideal for the development of PRO membranes, it is important to have the lowest reverse salt flux and higher water flux. In this research, it can be easily seen in Figure 5.16, where 1% CNC added PAN nanocomposite nanofiber TFC membranes provide the best results.

A further distinction was made between this research and the literature for the application of PRO in Table 5.2 in terms of water flux and reverse salt flux of membranes. The results show that fabricated membranes in this study have one of the highest J_w/J_s ratios in the literature.

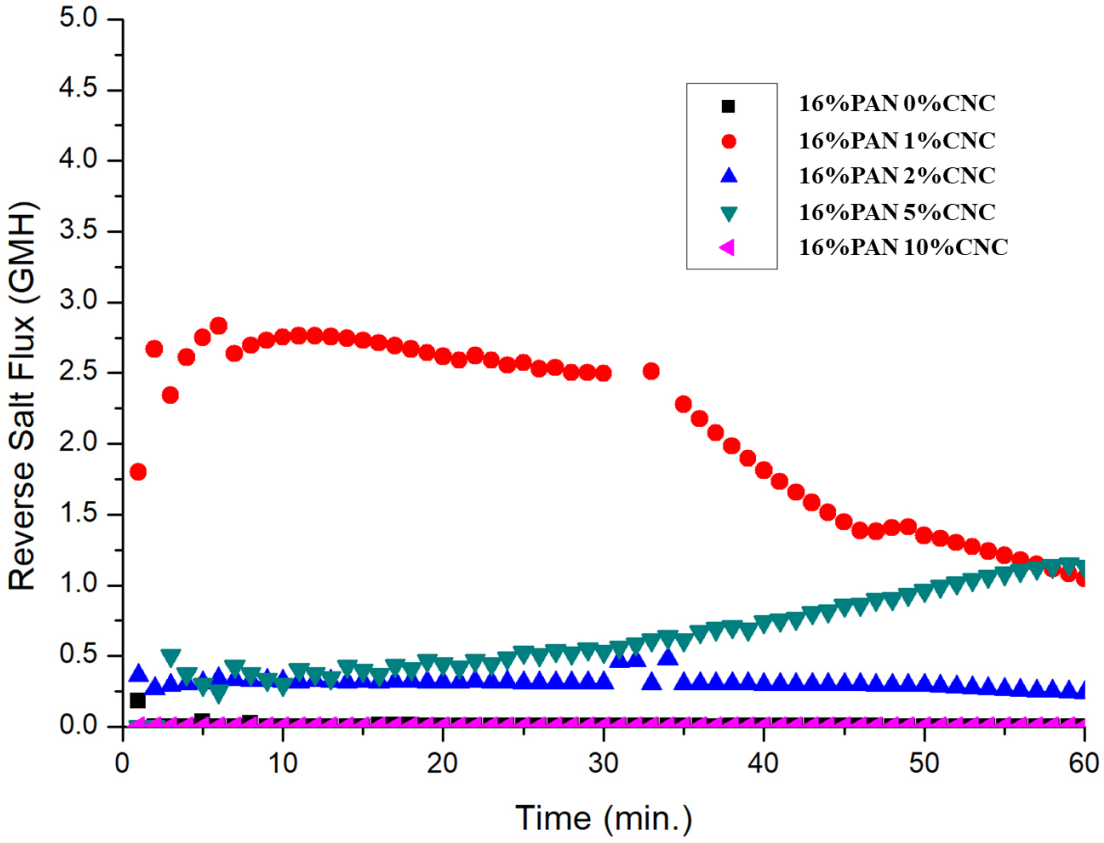


Figure 5.16 : Fabricated PAN/CNC nanocomposite PRO membranes water flux (Js).

5.5 Conclusions

Thin film nanocomposite (TFN) CNC added PRO membranes were successfully fabricated with tailor-made electrospinning machine. During operation, fabricated PRO membranes fulfill the needs of higher pressures. Increasing the amount of CNC has an impressive impact on the youngs' modulus that makes the PRO membrane stronger. FTIR spectra indicate that similar groups reacted with cellulose groups and modified the spectra, and it was observed that increasing the amount of CNC made the membrane more hydrophilic. Apart from the FTIR spectrum findings, it can be inferred that CNC content is compliant with PAN polymers. Morphology tests conducted using SEM equipment have shown that increasing the amount of CNC does not have a drastic impact on membrane formation until the addition of 10% of CNC. With regard to PRO

efficiency measurements, the %2 CNC addition to the PAN polymer matrix gives superior water flux and the lowest reversed salt flux. Comparing this research with the literature, it can be easily shown that PAN/CNC nanocomposite TFN membranes provide maximum water flux and one of the lowest inverted salt flux values.

Table 5.2 : Comparison of PRO performance of various TFC membranes with DI water as feed solutions.

Membrane	Water flux, J_W (PRO) (LMH)	Reverse salt flux, J_s (PRO) (gMH)	J_s/J_W (g/L)	J_w/J_s(g/L)	Draw solution	Ref.
PAN/CNC TFN membrane (2% CNC)	405.38	2.10	0.00518	193.03	1.0 M NaCI	This study
PAN/CNC nanocomposite TFC membrane (5% CNC)	300	1.50	0.005	200	1.0 M NaCI	(Pasaoglu et al, 2020)
FO flat-sheet membrane on sPSU	313	5.30	0.017	58.8	1.0 M NaCI	(Voisin et al, 2017)
CTA-ES HTI	8.10	20.03	2.47	0.4	1.0 M NaCI	(Voisin et al, 2017)
TFC-ES HTI	19.31	14.78	0.765	1.3	1.0 M NaCI	(Voisin et al, 2017)
Electrospun-PSf-based TFC with PET layer-before adding SDS	26	2.26×10^{-3}	0.00008	0.01150	1.5 M NaCI	(Bui et al, 2011)
Electrospun-PSf-based TFC with PET layer-after adding SDS	3.6	4.62×10^{-2}	0.0013	0.072	1.5 M NaCI	(Bui et al, 2011)
Electrospun-PSf-based TFC without PET layer-before adding SDS	24.0	8.63	0.359	2.78	1.5 M NaCI	(Bui et al, 2011)

Table 5.2 (continued) : Comparison of PRO performance of various TFC membranes with DI water as feed solutions.

Membrane	Water flux, J_W (PRO) (LMH)	Reverse salt flux, J_s (PRO) (gMH)	J_s/J_W (g/L)	J_w/J_s (g/L)	Draw solution	Ref.
Electrospun-PSf-based TFC without PET layer-after adding SDS	86.1	36.40	0.422	25.32	1.0 M NaCI	(Bui et al, 2011)
FO flat sheet membrane on cellulose ester substrate	128.8	19.40	0.15	6.67	2.0 M NaCI	(Ong et al, 2015)
FO flat sheet membrane on sulfonated polyphenylenesulfone (2.5 mole % direct sulfonation) supports	54	8.80	0.163	6.13	2.0 M NaCI	(Widjojo et al, 2013)
FO flat sheet membrane on PES/sPSf supports	47.5	12.40	0.261	3.83	2.0 M NaCI	(Wang et al, 2012)

6. CONCLUSION

Main conclusions and recommendations presented in the last section of each chapter. In this chapter, most important points and highlights will be given with a holistic approach. The main aim of the thesis was developing reinforced PRO membrane with high efficient specifications for desalination purpose. The main body of the thesis includes a literature, a review and two data chapters, which targeted improvement of the mechanical properties of the nanofiber based support, fabrication of thin film composite membrane and application in the process.

The following results were obtained in the thesis study:

- Even though membrane fabrication attemps are numerous in the literature, there is no information about the applicability of crystal nanocellulose (CNC) doped polymer mixture for electrospinning.
- The study proved that it is able to fabricate CNC doped polymeric mixtures for electrospinning applications specific to pressure retarded osmosis.
- The idea of of manufacturing CNC reinforced flat-sheet nanofiber pressure retarded osmosis membrane has emerged.
- High performance CNC doped reinforced nanofiber base support layer fabricated and characterized.
- Performance data showed that fabricated flat-sheet membrane have a water flux of 300 LMH and reverse salt flux as 1.5 gMH.
- This high performance was found to be due to the high hydrophilic property of CNC added to the polyacrylonitrile (PAN) polymer structure.
- Anovel approach studied for the first time in the literature as tubular pressure retarded osmosis membrane. Using same polymer/solvent/crystal nanocellulose ratio tubular nanofiber membranes were fabricated.
- In order to form tubular structure polyester hollow braided rope was used as substrate under nanofiber deposition.
- Performance data showed that fabricated tubular membrane have a water flux of 405.38 LMH and reverse salt flux as 2.10 gMH.

6.1 Future Works

According to the results obtained within the scope of this thesis, following recommendations can be given for further studies:

- Although the main purpose of this thesis is desalination from salty waters, it can be used for other sectors with different salinity streams.
- Crystal nanocellulose (CNC) is a versatile, cheap and abundant in nature. Surface hydroxyl groups and large specific area is reasonably high in CNC. Surface modifications of CNC may improve the compability with different matrices that gives the opportunity of controlling water flow through nanofibers.
- Crystal nanocellulose (CNC) doped in polyacrylonitrile (PAN) polymer is perfectly work with electrospinning process. Different polymer types may be applied with CNC in PRO processes.
- Since the nanofibers collected on a certain surface, it was showed that the adhesion of nanofibers on rough layer is easier than on a smooth surface. For this reason, production can be made by selecting a structure with a rough backing layer to increase the adhesion on the surface.

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- Best Oral Presentation Award, 6th MEMTEK International Symposium on Membrane Technologies and Applications, 18-20 November 2019, Turkey

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Articles

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