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Synthesis of recycled PET membranes for water vapor transport application

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Abstract

A new potential solution for PET plastic bottles recycling has been developed. This new step provides a breakthrough solution to broken down PET plastic waste. It is based on collecting plastic waste and reprocessing it into new membranes which are useful for gas separation.

Recycled PET polymer is recovered from water waste bottles. Asymmetric flat sheet membranes M1, M2, M3, M4 and M5 are prepared by the addition of PEG with same difference of the added quantity into recycled PET. Wet/dry gas precipitation phase technique is used for membranes preparation, the obtained thickness was in the range of 60-100 µm.

The fabricated membranes were investigated to evaluate the performance of PET membranes and the effect of hydrophilic PEG polymer addition on water vapor permeability and heat resistance. The morphology and water vapor permeability of prepared membranes were improved by the addition of PEG polymer.

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Abbreviations

Å	**Angstrom, unit of length**	**10^{-10} m**
A	**Test area (cup mouth area)**	**m^2**
CA	**Cellulose acetate**	
°C	**Degree Celsius**	
cm	**Centimeter, unit of length**	**10^{-2} m**
COO	**Ester functional group**	
COOH	**Carboxyl functional group**	
D	**Dialysis**	
DMPC	**Dynamic Moisture Permeabilation Cell**	
EPWG CET	**Etablissement Public de Wilaya de Gestion des Centres d'Enfouissement Technique**	
IUPAC	**International Union of Pure and Applied Chemistry**	
H_2O	**Water formula**	
G	**Weight change, Water Mass Lost**	**g**
GP	**Gas permeation**	
G/t	**Flux of membrane’s mass lost**	**g/min**
l	**Thickness of membranes**	**µm**
M1	**Membrane sheet (100PET/0PEG)**	
M2	**Membrane sheet (90PET/10PEG)**	
M3	**Membrane sheet (80PET/20PEG)**	
M4	**Membrane sheet (70PET/30PEG)**	
M5	**Membrane sheet (60PET/40PEG)**	
mm	**Millimeter, unit of length**	**10^{-3} m**
MF	**Microfiltration**	
NF	**Nanofiltration**	

NIPS	No-solvent Induced Phase separation	
pm	Pico-meter, unit of length	10^{-12} m
OH	Hydroxyl functional group	
P	Permeance of membranes	$g.s^{-}1.m^{-2}Pa^{-1}$
PET (PETP)	Polyethylene terephthalate	
PSE	Polyethersulfone	
PSF	Polysulfone	
PV	Pervaporation	
PVDF	Polyvinylidenefluoride	
Ps	Saturation vapor pressure	6254,436 Pa
R1	Relative humidity in the water dish	%
R2	Relative humidity at the furnace	%
RO	Reverse osmose	
t	Time	min
TR	Transmission rate	$g.s^{-1}.m^{-2}$
UF	Ultrafiltration	
VIPS	Vapor Induced Phase Separation	
WVP	Water Vapor Permeability	$g.\mu m.s^{-1}m^{-2}Pa^{-1}$
WVT	Rate of water vapor transmission	$g.h^{\cdot 1}.m^{-2}$
µm	Micrometer, unit of length	10^{-6} m
ΔP	Vapor pressure difference	Pa
ΔC	Difference (diffusion) of concentration	$g.ml^{-1}$
ΔT	Difference of temperature	°C
ΔE	Difference of Energy	Joule

Introduction

Membrane technology has been leading a strategic role in the sustainable development of many industries. Membrane technology is greatly preferred and applied in various sectors like in the medical field, bio-separation, bio-refinery, food and beverage industry, megaproject water treatment plant, water reclamation with membrane bioreactor, energy generator, and gas separation[1]. Due to many merits it offers such as low energy consumption, ease of scaling-up, can be combined with other separation processes, and needless of additional chemicals during the filtration process[2].

Membrane base-materials are generally sourced from organic compounds such as polymers. Some of the frequently used polymers as membrane material are polyethersulfone (PES), cellulose acetate (CA), polysulfone (PSf), polyvinylidene fluoride (PVDF), and polyethylene terephthalate (PET). The characteristics of each of these polymers are different which will accordingly affect the characteristics of the fabricated membranes, such as hydrophilicity, flexibility, and fouling resistance that will also affect the operation performance[3].

The pores are responsible for the various properties that can make them viable for a particular application, both to separate particles and to fractionate molecules of different molar masses. The membranes can act as a selective barrier like a filter, they can separate materials that with a regular filter would not be possible because it lacks adequate capacity for this type of process[4][5].

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering, stretching, track etching and phase inversion. The final morphology of the membrane obtained varies greatly, depending on the properties of materials and the process conditions utilized[6].

The phase inversion is the method that is being very used to obtain polymeric membranes, which a polymer solution is spread as a thin film on a glass plate or extruded as a hollow fiber, and then precipitated in a non-solvent bath[7][8]. The membrane is formed by the destabilization of the solution and the polymer precipitation. The most successful solvent systems used for dissolution of polymers include chlorinated phenols and strong organic acids [9]. In many applications a mixed solvent system, is used as it is often found that only a small amount of the acid is required for solubility. Indeed for many systems once there is sufficient acid to dissolve the polymer[10].This technique allows large morphological change from small variations made in parameters used during the membranes preparation process[11].

The polymeric membranes have several advantages, and they have been used in various applications in industrial processes, such as in processes of separation, purification and fractionation of various industrial branches[7][12]. The main processes in which membranes are being used are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis (D), gas permeation (GP) and pervaporation (PV). The efficiency and application of the membranes will depends on the morphology that it will present and as well as the nature of the material that constitutes[13][14]

For greater efficiency in production and application of the membranes, the surface modification is an approach that has been widely exploited to improve the fouling resistance in water purification from membranes. Thus, it is necessary to introduce a factor that can improve the characteristics and efficiency of the membrane[15].

Commercial polymers certainly have an expensive price which increases membrane production cost. Therefore, it is necessary to create a membrane with an appropriate composition to produce an economic membrane with superior characteristics. One of the ways to reduce the consumption of commercial polymers and membrane manufacturing costs is by utilizing polymer-based waste materials[16]. Advanced technology in food and beverage sectors currently encourage the use of polyethylene terephthalate (PET) as plastic packaging.

Polyethylene Terephtalate has a strong and durable structure which lead it difficult to degrade in the environment[17], its continuous use leads to an increment of a waste of PET bottles and cause an environmental poullution[18]. However, plastic bottle can be potentially re-used by utilizing the PET as the main material of the polymeric membrane[19] to support a green technology that minimizes the environmental pollution and reduce the cost of manufacturing membranes.

The manufacture of PET membrane from the waste plastic bottle had previously been investigated by Rajesh and Murthy[19]. The resulting membrane had weak mechanical and hydrophilicity properties. Therefore, an additional modification is needed to improve its characteristics, for instance by combining it with other polymeric material to produce composite membrane.[20][21][22]

In Mostaganem, referenced to the table below, a significant data shows a rising consumption of waste materials: wood, Metals, PET, ect….

Table 1 : Recovered products (Plastics, papers, wood,...) in EPWG of Mostaganem

	2014	2015	2016	2017	2018	TOTAL
Type of Product	**Quantity (kg)**	**Quantity (kg)**	**Quantity (kg)**	**Quantity (kg)**	**Quantity (kg)**	**Quantity (kg)**
PET	26700	14500	30270,5	328343,1	613635	1013448,6
Other plastics	10120	3000	754,8	17683,3	2636	34194,1
Papers	0	85960	103050	27900	47220	264130
Aluminum	0	0	0	0	0	0
Packing tarpaulin	0	5640	2814,3	36079,4	51324	95857,7
Wood	0	0	0	0	0	0
Blankets	6240	28920	14120	0	0	49280
Iron	1180	0	0	0	0	1180

PET bottles consumption was presented higher percentage compared to other wastes, in year 2018 was 613635 Tons, twice consumption of PET in 2017. This situation will create serious environmental problems that require much more effort to be exerted to look for practical solutions for the disposal of plastic waste through recycling.

In the present work, PET polymer is successfully recycled from waste plastic bottles. A selective membrane material was made. An asymmetric flat sheet membranes of hydrophobic PET polymer blended with different percentages of hydrophilic material and appropriate film casting conditions have been successfully fabricated via phase inversion induced by dry and immersion precipitation technique.

An investigation to evaluate the performance of PET membrane and the addition effect of the hydrophilic material on the selectivity and permeability for water vapor application.

CHAPTER I

MEMBRANE TECHNOLOGY

I.1 Introduction

Membrane separation processes offer a number of advantages in terms of less energy requirements, environmental impacts and capital investments. The processes are also simple and easy to operate and need compact equipment. Hence, they have recently demonstrated a significant industrial role in terms of economical considerations and been used in a wide range of applications such as supply of high quality water, removal or recovery of toxic or valuable components from various industrial effluents and also food and pharmaceutical industries [23][24][25]. The most important part of a membrane separation process is the membrane itself and polymeric membranes are the most common ones used in the membrane processes[26].

I.2 Definition

Membrane technology covers a number of different processes for the transport of substances between two fractions with the help of permeable membranes [27]. Membranes used in membrane technology may be regarded as selective barriers separating two fluids and allowing the passage of certain components and the retention of others from a given mixture, implying the concentration of one or more components. The driving force for the transport is generally a gradient of some potential such as pressure, temperature, concentration or electric potential [27].

One of the particular advantages of membrane separation process is that it relies on a physical separation, usually with no addition of chemicals in the feed stream and without phase change [28]. Moreover it can be operated without heating. Therefore, this separation process is energetically usually lower than conventional separation technologies (i.e., distillation, crystallization, adsorption...). What’s more, it responds more efficiently to the requirements of process intensification strategy because it permits drastic improvements in industrial production, substantially decreasing the equipment-size/production-capacity ratio, energy consumption, and/or waste production so resulting in sustainable technical solutions [29].

Although typically thought to be expensive and relatively experimental, membrane technology is advancing quickly becoming less expensive, improving performance, and extending life expectancy. It has led to significant innovations in both processes and products in various industrial sectors (e.g. chemical, pharmaceutical, biotechnological, food sectors, etc) over the past few decades.

I.3 Membrane flow configurations

Membrane systems can be operated in various process configurations. There are two main flow configurations of membrane processes: dead-end and crossflow filtrations, as presented in **Figure I-1**. In a conventional filtration system, the fluid flow, be it liquid or gaseous, is perpendicular to the membrane surface. In this dead-end filtration, there is no recirculation of the concentrate, thus solutes are more probable to deposit on the membrane surface, and the system operation is based on 100% recovery of the feed water. In crossflow filtration, the feed flow is tangential to the membrane surface and then divided into two streams. The retentate or concentrate (solution that does not permeate through the surface of the membrane) is recirculated and blended with the feed water, whereas the permeate flow is tracked on the other side [30][31].

Both flow configurations offer some advantages and disadvantages. The dead-end membranes are relatively less costly to fabricate and the process is easy to implement. The main disadvantage of a dead-end filtration is the extensive membrane fouling and concentration polarization, which requires periodic interruption of the process to clean or substitute the filter [32]. The tangential flow devices are less susceptible to fouling due to the sweeping effects and high shear rates of the passing flow.

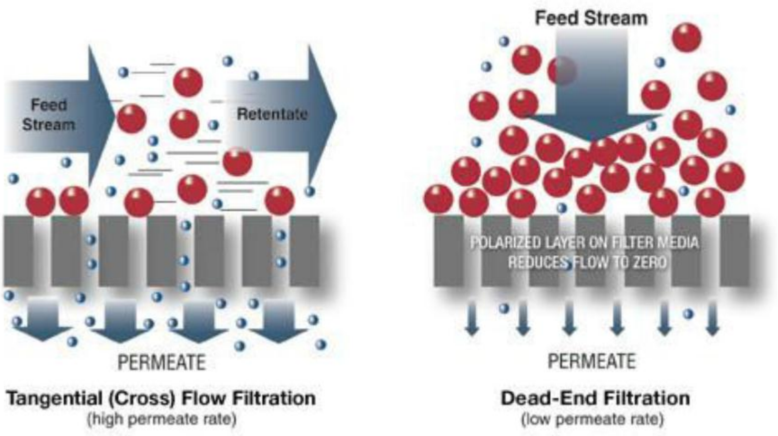


Figure I-1: Membrane flow configurations [33]

I.4 Flow transport through a membrane

The first theory of the permeation through polymers was done by Thomas Graham in 1866 where he presents the solution-diffusion process. Graham stated that a gas would absorb in one side of a polymer membrane, followed by diffusion through the membrane and adsorb out on the other side of the membrane. [34]

The transport through a membrane occurs when a driving force acting on the membrane in the feed side is higher than the driving force at the permeate side[35], seen in **Figure I-2**.

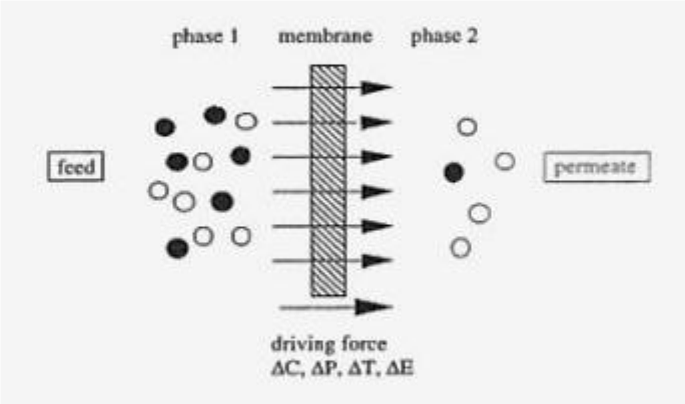


Figure I-2: The transport of a gas from phase 1, through a membrane and into phase 2. [8]

I.4.1 Selectivity

Membrane separation occurs because of differences in kinetic diameters (Table I-1) and shape, chemical properties, or electrical charge of the substances to be separated; for example, microporous membranes control separation by size and discrimination. In the case of porous membranes, species small enough to enter the pores are transported by convective flow while non-porous membranes rely on sorption and diffusion through the membrane as discussed earlier. Furthermore, membranes do not have a sharp separation between species[36].

Table I-1: Kinetic diameters of various gases

Molecule		Molecular weight	Kinetic Diameter (pm)	Ref	Molecule		Molecular Weight	Kinetic Diameter (pm)	Ref
Name	Formula				Name	Formula			
Ammonia	NH_3	17	260	[37]	Hydrogen bromide	HBr	81	350	[37]
Helium	He	4	260	[38]	Hydrogen sulfide	H_2S	34	360	[38]
Water	H_2O	18	265	[39]	Sulfur dioxide	SO_2	64	360	[37]
Hydrogen	H_2	2	289	[39]	Nitrogen	N_2	28	364	[39]
Chlorine	Cl_2	70	320	[37]	Carbon monoxide	CO	28	376	[38]
Hydrogen chloride	HCl	36	320	[37]	Methane	CH_4	16	380	[39]
Carbon dioxide	CO_2	44	330	[37]	Ethylene	C_2H_4	28	390	[38]
Nitrous oxide	N_2O	44	330	[38]	Propane	C_3H_8	44	430	[38]
Oxygen	O_2	32	346	[39]	Propylene	C_3H_6	42	450	[38]
Bromine	Br_2	160	350	[37]	Benzene	C_6H_6	78	585	[40]

I.4.2 Diffusivity

Diffusion is the kinetic part of the solution-diffusion model and occurs because of concentration difference on both sides of the membrane. The diffusivity in a polymer is dependent of the geometry and size of the penetrant and the free volume in the polymer matrix. Generally, the diffusivity also depends on the temperature and in some cases on the solute concentration.[34][35]

Movement of solutes across membranes can be divided into two basic types: passive diffusion and active transport [41]. **Passive diffusion** requires no additional energy source other than what is found in the solute's electrochemical (concentration) gradient and results in the solute reaching equilibrium across the membrane. Passive diffusion can be facilitated passive diffusion where the solute crosses the membrane at specific locations where diffusion is assisted by solute-specific facilitators or carriers. **Active transport** requires additional energy, and results in a non-equilibrium, net accumulation (uptake) of the solute on one side of the membrane. The basic types of membrane transport, simple passive diffusion, facilitated diffusion (by channels and carriers) and active transport are summarized in **Figure I-3** [42].

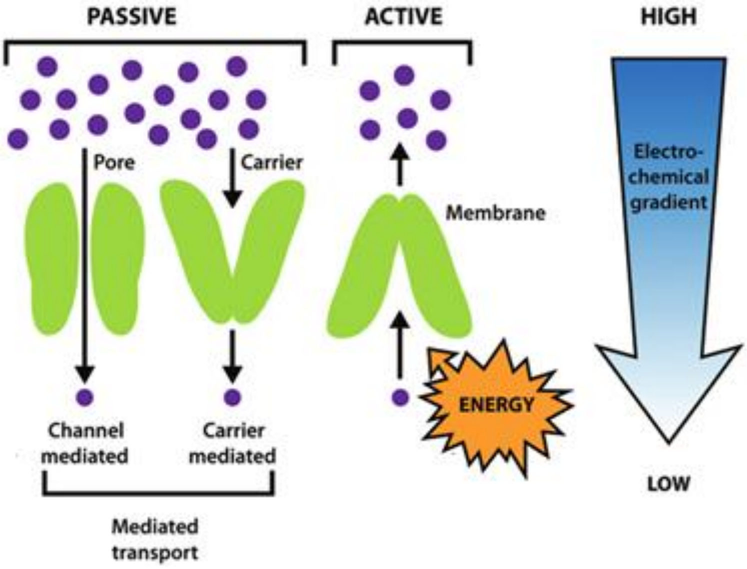


Figure I-3: Basic types of membrane transport: passive diffusion and active transport.

I.4.3 Permeability

The permeability is the intrinsic ability of a membrane material to control the rate at which molecules are allowed to permeate through the membrane. It dependents of both the diffusivity and the solubility in the polymer. Physical factors like temperature, humidity and the structure will affect the permeability coefficient and must be considered[34][35].

I.5 Classification of membranes

I.5.1 Classification according to the geometry of the membranes

There are four main types of modules: plate-and-frame, tubular, spiral wound, and hollow fiber[44] (**Figure I-4**). The plate-and-frame module is the simplest configuration, consisting of two end plates, the flat sheet membrane, and spacers. In tubular modules, the membrane is often on the inside of a tube, and the feed solution is pumped through the tube[44]. Hollow fiber modules used for seawater desalination consist of bundles of hollow fibers in a pressure vessel, they can be also used in a bore-side feed configuration where the feed is circulated through the fibers[44].

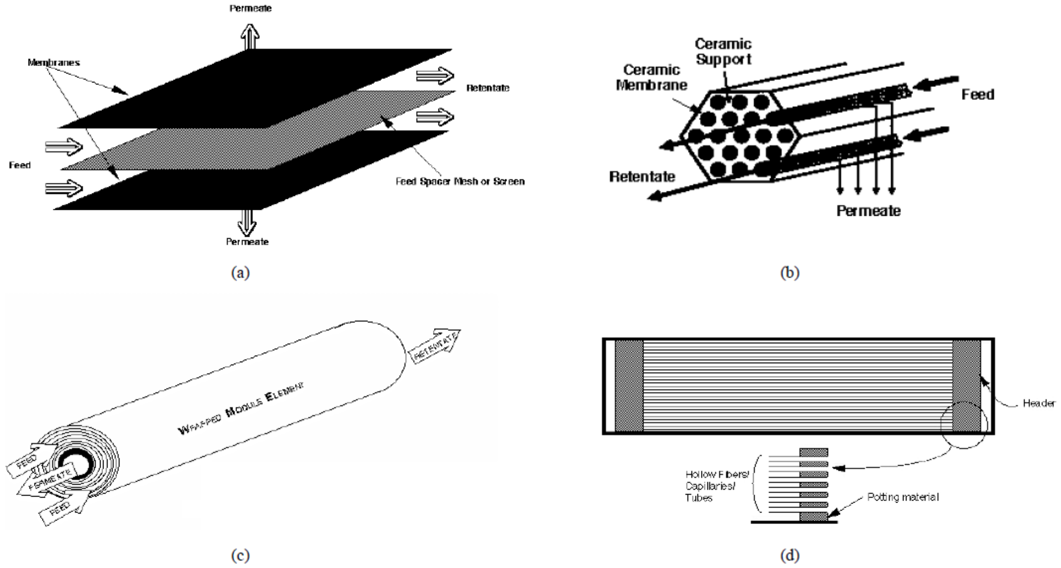


Figure I-4: Schematic of:

a) Plate and frame b) Tubular

c) Spiral wound d) Hollow fiber modules**[45].**

I.5.2 Classification according to chemical nature:

Most MF, UF, RO, and NF membranes are synthetic organic polymers. MF and UF membranes are often made from the same materials, but they are prepared under different membrane formation conditions so that different pore sizes are produced[46].

Typical MF and UF polymers include polyvinylidene fluoride, polysulfone, polyacrylonitrile and polyacrylonitrile-polyvinyl chloride copolymers[44]. Polyether sulfone is also commonly used for UF membranes [44]. MF membranes also include cellulose acetate-cellulose nitrate blends, nylons, and polytetrafluoroethylene [44]. RO membranes are typically either cellulose acetate or polysulfone coated with aromatic polyamides[44]. NF membranes are made from cellulose acetate blends or polyamide composites like the RO membranes, or they could be modified forms of UF membranes such as sulfonated polysulfone[47].

Membranes can also be prepared from inorganic materials such as ceramics or metals[44]. Ceramic membranes are microporous, thermally stable, chemically resistant, and often used for microfiltration[44]. Metallic membranes are often made of stainless steel and can be very finely porous. Their main application is in gas separations, but they can also be used for water filtration at high temperatures or as a membrane support[48].

I.5.3 Classification according to morphology

Membranes are generally classified as isotropic or anisotropic. Isotropic membranes are uniform in composition and physical nature across the cross-section of the membrane. Anisotropic membranes are non-uniform over the membrane cross-section, and they typically consist of layers which vary in structure and/or chemical composition:

I.5.3.1 Isotropic membranes: Can be divided into various subcategories. For example, isotropic membranes may be microporous. Microporous membranes are often prepared from rigid polymeric materials with large voids that create interconnected pores[44]. The most common microporous membranes are phase inversion membranes (**Figure I-5 a**) [44]. These are produced by casting a film from a solution of polymer and solvent and immersing the cast film in a nonsolvent for the polymer.

Another type of microporous membrane is the track-etched membrane (**Figure I-5 b**)[44]. This type of membrane is prepared by irradiating a polymer film with charged particles that attack the polymer chains, leaving damaged molecules behind. A less common microporous membrane is an expanded-film membrane (**Figure I-5 c**)[44].
Expanded film membranes are oriented crystalline polymers with voids created by an extrusion and stretching process.

Isotropic membranes can also be dense films which either lack pores or contain pores that are so small as to render the membrane effectively non-porous. These films are prepared by solution casting followed by solvent[44].

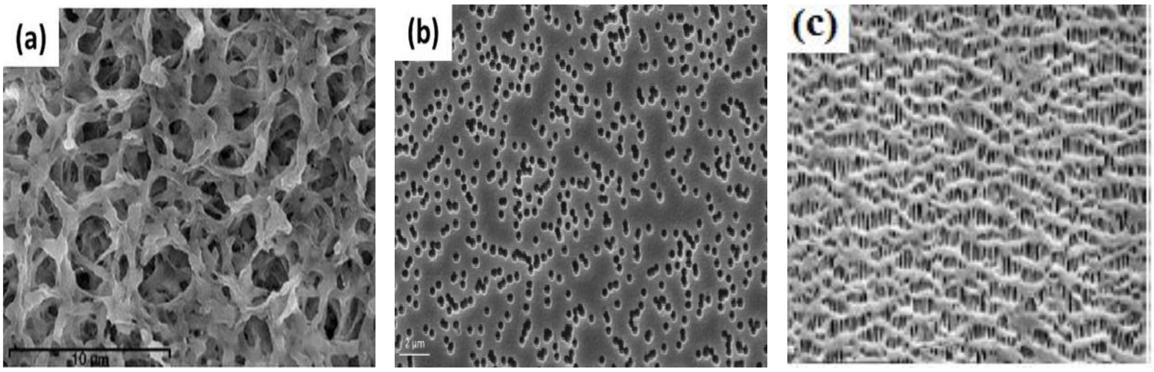


Figure I-5: SEM images showing top surfaces of :

a) Phase inversion membrane[48] b) Track-etched membrane[48] c) Expanded film membrane[48]

I.5.3.2 Anisotropic membranes: There are two main types of anisotropic membranes: phase separation membranes and thin film composite membranes[44]:

The phase-separated membranes are homogeneous in chemical composition but not in structure, produced via phase inversion techniques such as those described above, except that the pore sizes and porosity vary across the membrane thickness (**Figure I-6 a**). They often consist of a rather dense layer of polymer on the surface of an increasingly porous layer.

Thin film composite membranes are both chemically and structurally heterogeneous (**Figure I-6 b**)[44]. Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. They can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment[44]

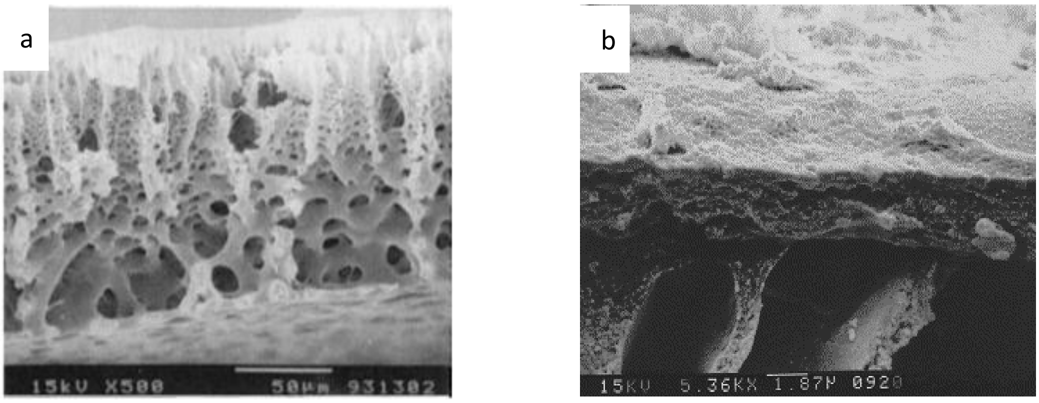


Figure I-6: SEM images of: a) cross-section of an anisotropic microporous membrane[49]
b) cross-section of a thin-film composite membrane [50].

I.6 Types of membranes:

In the field separation of liquid solutions by membrane processes, four main categories have been identified microfiltration (MF), ultrafiltration (UF), nano filtration (NF) and reverse osmosis (RO) which are distinguished by the membrane’s selectivity and subsequent retained particles in each process.

I.6.1 Microfiltration (MF): Microfiltration membrane processes are extensively used for in different industrial fields. One major use of MF processes contains the treatment of potable water supplies. The MF process is the key step in the primary disinfection in the membrane filtration series for production of pure water. The initial stream might contain resistant pathogens to the traditional disinfectants (chlorine for example). MF processes offer a physical separation of these particles with use of the membrane as barriers [51]. Another useful application for MF processes includes the cold sterilization both in food sector and pharmacy[52]. This is one main advantage compared to traditional heating methods in which there is major loss of effectiveness for pharmaceuticals and flavor and freshness modification of food products. In past decades, MF processes have also got interest in petroleum refining, dairy industry, biochemical and bioprocessing applications [51].

I.6.2 Ultrafiltration (UF): In ultrafiltration processes, suspended solids and solutes with molecular weight higher than 300 kDa are retained.Therefore UF processes can be useful for retaining proteins, antibiotics and certain ions [51], [52]. The membrane pore size varies between 2 and 100 nm and the applied pressure gradient is larger than 1 bar.In theory, there is a clear difference between microfiltration and ultrafiltration pore sizes, however these techniques can be combined technically in different domains in order to minimize the particle accumulation to the membrane surface and consequent energy loss.

I.6.3 Nanofiltration (NF): The NF processes are known for retaining small particles and dissolved molecules, specially multivalent ions in complex solutions. The processes are applied mostly for treating the surface water and fresh groundwater in order to softening (removal of multivalentions) the water or retaining natural and synthetic organic matter. [55],[56]. NF membranes properties are between reverse osmosis (RO) membrane and UF membranes. The membrane pores are less than 1 nom and the applied pressure gradient is in the range of 4 and 20 bar[57].

I.6.4 Reverse osmosis (RO): Reverse osmosis membranes are dense membranes without distinct pores. In these processes monovalent ions (< 10 Å) can be retained[57]. The applied pressure gradient range is between 40 and 100 bar. In RO processes, the solvent is forced by pressure gradient to pass through the dense membrane from a region of high solute concentration (retentate) to a region of low solute concentration (permeate). The most important application of RO is for desalination of sea water and brackish waters and to production of pure water. Recently, RO processes are also used in food sector for concentrating the food liquids (fruit juice for example) because of their low operational costs compared to convectional heat treatment/vacuum evaporation methods [58][59][60].

I.7 Effects of the phase inversion on membrane's proprieties

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering, stretching, track etching and phase inversion. The final morphology of the membrane obtained varies greatly, depending on the properties of materials and the process conditions utilized [61]. The phase inversion is one of the common techniques used for the development of asymmetric polymer membranes [62][63]; It's a demixing process in which initially homogeneous polymer solution is transformed from a liquid state to a solid state in a controlled manner [64]. The membrane structure, properties, and chemical interaction depend on the choice of polymer, as does the choice of additives used in the casting solution [65][66], the solvent and non-solvent, bath temperature and precipitation time [67][68][69]

There are various methods introduced in literature for phase inversion including non-solvent immersion, non-solvent vapors technique, thermal practice, quenching, etc [70]. Nowadays, the most common phase separation method for manufacturing polymeric membranes is NIPS (Non-solvent Induced Phase Separation) method, which involves non-solvent intake into a polymer/solvent system. Water is classically used as the non-solvent and NIPS can be divided in two processes:

- **Wet process (or immersion process)** that consists of immersing the polymer solution (collodion) into a water bath[71][72][73].
- **VIPS (Vapor Induced Phase Separation)** process where the collodion is exposed to humid vapors [74][75] . VIPS process allows preventing the formation of macrovoids since the mass transfers occurring during the process, i.e. water intake and solvent extraction, are strongly reduced [76][77][78].

In immersion process, there are three components: polymer, solvent, and non-solvent [79].

The polymer is dissolved in a suitable solvent. The resulting polymer solution is casted on a suitable support and is immersed in the coagulation bath containing a nonsolvent (usually water). The solvent penetrates into the nonsolvent and the nonsolvent penetrates in the polymer solution. This exchange continues until demixing occurs. As a result, a homogeneous polymer solution turns into two phases. One of them is the polymer-rich phase, which is a membrane with an asymmetric structure, and the other is the liquid-rich phase [80][81].

CHAPTER II

RECYCLED POLYMERS

II.1 Introduction

In the present world of consumerism, plastic and polymers have been the prime choice of materials in packaging industries. There are a variety of plastic among which not a single variety is biodegradable [82]. Therefore, the majority of polymers manufactured today will persist for at least decades or probably centuries. Even though the plastic having the quality of degradation, may be irresistible for a considerable amount of time depending on various local environmental factors, as rates of degradation depend primarily on physical factors; such as, levels of ultraviolet light exposure, oxygen and temperature.[83]

Plastic recycling is clearly a waste-management strategy which is receiving increasing attention that can reduce environmental impact and resource depletion. It can decrease energy and material use per unit of output and therefore yield improved eco-efficiency [84]

II.2 Polymers

II.2.1 Définition of polymer

A polymer is a compound of high molecular weight, buildup from a simple monomer repeated throughout a chain. Polymerization is a polyreaction where the polymer chains are produced and due to the variation of monomers, polymers are further divided into different classes.[85]

II.2.2 The Structure of Polymers

Polymers can be homopolymers or co-polymers[86]:

- **Homopolymers** are a polymer connected by the same monomer throughout its chain.
- **Co-polymers** are two or more different polymers connected in the same polymer chain.

The structure of a polymer can either be linear, branched or crosslinked, seen in **Figure II-1**.

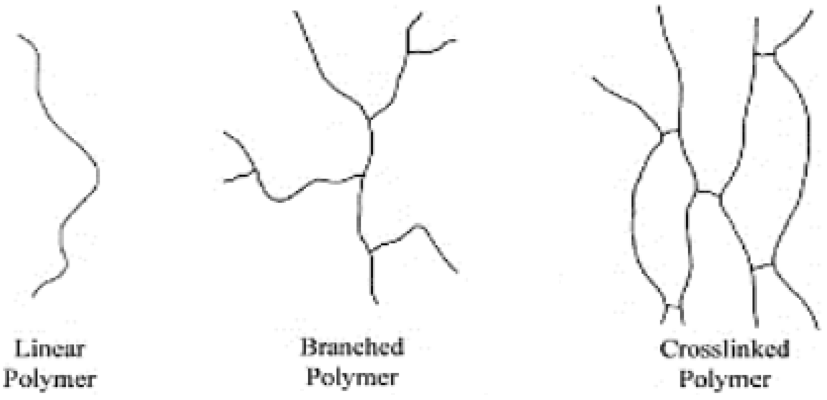


Figure II-1: The different structures in linear-, branched- and cross-linked polymers. [86]

II.2.3 Classification of Polymers

The three main classes polymers can be divided into are; Thermosets, elastomers and thermoplastics[86][87]:

- **Thermoplastic** can be moulded to shape by the application of heat and pressure in the molten shape and can be reshaped once formed. This type of polymer is not cross-linked but generally consists of linear polymer chains.
- **Thermoset** are generally polymerised in their final state and cannot be reshaped by applying heat. The chains in this type of polymer are generally covalently cross-linked.
- **Elastomers** are polymers that either is made from thermoplastic or thermoset, with the ability of frequently stretching to over twice its size with no permanent deformation.

II.3 Plastics

II.3.1 Definition of plastic

Plastics are generally defined as "Material containing an organic substance of large molecular weight (polymers) that is solid in its final condition and that, at some earlier time, was shaped by flow[88].

II.3.2 Properties of plastics

As a result of having properties such as environment resistance, low density, high strength, user friendly design, etc., plastics are very functional [89][90].
Plastic manufacturing cost is not so high because of its simple mass production. Due to their corrosion resistance, plastics usage in our life, in volume, is much higher than that of aluminum and other metals [90]. Some main reasons which make plastics valuable are:

- A wide range of additives, fillers and reinforcements, copolymerization, compounding and adjusted operating condition causes each plastic to be tailored for a specific use.
- Several processing methods lead to have various kinds of plastic products from very small ones to very large ones.
- Diverse manufacturing systems make it possible to produce plastic products with the lowest cost range[90][91].

II.4 Recycled plastics (Recycled polymers)

There are seven plastic types based on their chemical composition. They vary in transparency and strength as well as other characteristics[92].

Most of the plastic bottles have a figure inside a triangular recycling symbol that is printed at the bottom of the bottle. The description of the recycled plastic in the table II-1

Table II-1: Description of recycling symbol code [93].

Codes	**Descriptions**	**Properties**	**Packaging Applications**	**Recycled Products**
	Polyethylene Terephthalate (PET, PETE). PET is clear, tough, and has good gas and moisture barrier properties. Commonly used in soft drink bottles and many injection molded consumer product containers. Other applications include strapping and both food and non-food containers. Cleaned, recycled PET flakes and pellets are in great demand for spinning fiber for carpet yarns, producing fiberfill and geo-textiles. Nickname: Polyester.	Clarity, strength, toughness, barrier to gas and moisture, resistance to heat	Plastic soft drink, water, sports drink, beer, mouthwash, catsup and salad dressing bottles. Peanut butter, pickle, jelly and jam jars. Ovenable film and ovenable prepared food trays.	Fiber, tote bags, clothing, film and sheet, food and beverage containers, carpet, strapping, fleece wear, luggage and bottles.
	High Density Polyethylene (HDPE). HDPE is used to make bottles for milk, juice, water and laundry products. Unpigmented bottles are translucent, have good barrier properties and stiffness, and are well suited to packaging products with a short shelf life such as milk. Because HDPE has good chemical resistance, it is used for packaging many household and industrial chemicals such as detergents and bleach. Pigmented HDPE bottles have better stress crack resistance than unpigmented HDPE bottles.	Stiffness, strength, toughness, resistance to chemicals and moisture, permeability to gas, ease of processing, and ease of forming.	Milk, water, juice, cosmetic, shampoo, dish and laundry detergent bottles; yogurt and margarine tubs; cereal box liners; grocery, trash and retail bags.	Liquid laundry detergent, shampoo, conditioner and motor oil bottles; pipe, buckets, crates, flower pots, garden edging, film and sheet, recycling bins, benches, dog houses, plastic lumber, floor tiles, picnic tables, fencing.
	Vinyl (Polyvinyl Chloride or PVC): In addition to its stable physical properties, PVC has excellent chemical resistance, good weatherability, flow characteristics and stable electrical properties. The diverse slate of vinyl products can be broadly divided into rigid and flexible materials. Bottles and packaging sheet are major rigid markets, but it is also widely used in the construction market for such applications as pipes and fittings, siding, carpet backing and windows. Flexible vinyl is used in wire and cable insulation, film and sheet, floor coverings synthetic leather products, coatings, blood bags, medical tubing and many other applications.	Versatility, clarity, ease of blending, strength, toughness, resistance to grease, oil and chemicals.	Clear food and non-food packaging, medical tubing, wire and cable insulation, film and sheet, construction products such as pipes, fittings, siding, floor tiles, carpet backing and window frames..	Packaging, loose-leaf binders, decking, paneling, gutters, mud flaps, film and sheet, floor tiles and mats, resilient flooring, cassette trays, electrical boxes, cables, traffic cones, garden hose, mobile home skirting.
	Low Density Polyethylene (LDPE).Used predominately in film applications due to its toughness, flexibility and relative transparency,	Ease of processing, strength, toughness,	Dry cleaning, bread and frozen food bags, squeezable	Shipping envelopes, garbage can liners, floor tile,

4 PE-LD	making it popular for use in applications where heat sealing is necessary. LDPE is also used to manufacture some flexible lids and bottles and it is used in wire and cable applications	flexibility, ease of sealing, barrier to moisture.	bottles, e.g. honey, mustard.	furniture, film and sheet, compost bins, paneling, trash cans, landscape timber, lumber
5 PP	Polypropylene (PP). Polypropylene has good chemical resistance, is strong, and has a high melting point making it good for hot-fill liquids. PP is found in flexible and rigid packaging to fibers and large molded parts for automotive and consumer products.	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Catsup bottles, yogurt containers and margarine tubs, medicine bottles	Automobile battery cases, signal lights, battery cables, brooms, brushes, ice scrapers, oil funnels, bicycle racks, rakes, bins, pallets, sheeting, trays.
6 PS	Polystyrene (PS). Polystyrene is a versatile plastic that can be rigid or foamed. General purpose polystyrene is clear, hard and brittle. It has a relatively low melting point. Typical applications include protective packaging, containers, lids, cups, bottles and trays.	Versatility, insulation, clarity, easily formed	Compact disc jackets, food service applications, grocery store meat trays, egg cartons, aspirin bottles, cups, plates, cutlery.	Thermometers, light switch plates, thermal insulation, egg cartons, vents, desk trays, rulers, license plate frames, foam packing, foam plates, cups, utensils
7 O	Other. Use of this code indicates that the package in question is made with a resin other than the six listed above, or is made of more than one resin listed above, and used in a multi-layer combination.	Dependent on resin or combination of resins	Three and five gallon reusable water bottles, some citrus juice and catsup bottles.	Bottles, plastic lumber applications.

II.5 Polyethylene Terephthalate

II.5.1 Defintion

According to IUPAC polymer nomenclature, the systematic structure based name of this polymer is poly(oxyethylene oxyterephthaloyl). The common name is poly(ethylene terephthalate) and the abbreviation commonly used in literature is PET or PETP.[94][95]

Polyethylene terephthalate (PET) is an aromatic, thermoplastic, and semicrystalline polymer, and the most common type of polyester used commercially. It is also one of the most recycled plastics in the market. [96]

II.5.2 Structure of Poly(Ethylene Terephthalate)

PET is generally produced by the polymerization of ethylene glycol and terephthalic acid (figure)[97]. Ethylene glycol is a diol; an alcohol with a molecular structure that contains two hydroxyl (OH) groups, and terephthalic acid is a dicarboxylic aromatic acid; an acid with a molecular structure that contains a large, six-sided carbon (or aromatic) ring and two carboxyl (COOH) groups. When subjected to heat in the presence of chemical catalysts, ethylene glycol, and terephthalic acid produce PET in the form of a molten, viscous mass that can be spun directly to fibers or solidified for later processing as a plastic (under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester (COO) groups, which serve as the chemical links joining multiple PET units together into long-chain polymers) [98].

II.5.3 Proprieties of PolyEthylene Terephtalate:

Poly(ethylene terephthalate) is the most important thermoplastic terephthalate with high-performance characteristics including high glass transition temperature, superior mechanical properties, and chemical resistance. Other characteristics of PET include relatively low cost, high transparency, and moderate recyclability[96]. PET has low moisture absorption, allowing the material to maintain excellent dimensional stability through extremes of temperature and high humidity[99]. The main reasons for its popularity are the properties of glass-like transparency coupled with adequate gas barrier properties for retention of carbonation. Also it exhibits a high toughness-weight property ratio which allows lightweight, large capacity safe unbreakable containers[100].

Table II-2: Properties of PET plastic.[101]

Properties	**Values**
Molecular formula	$C_{10}H_8O_4$
Molar mass	Variable
Density	1.38g/cm 3 (20°c) amorphous :1.370 g/cm 3 singale crystal :1.455g/cm3
Melting point	250 °C
Boiling point	350°C decomposes
Solubility in water	Practically insoluble
Thermal conductivity	0.15-0.24 w/m/k
Refractive index	1.57-1.58w/m/k
Specific heat capacity	1.0Kj (kg k)

Due to these attributes, PET finds industrial applications such as fibers, films, bottles, and engineering plastics. The properties of the PET plastics are listed in the Table 2.[101][102]

CHAPTER III

EXPERIMENTAL PART

III.1 Introduction

Many polymeric membranes used today in separation process are composed of a rather asymmetric structure, consisting of a very thin selective layer on a highly porous thick sublayer. This type of membranes is produced by the phase-inversion process, which is a multistep process involving: solution preparation, film casting, partial solvent evaporation, coagulation and sometimes heat post-treatment. The morphology and performance, and mechanical properties of the membranes are strictly related to the above preparation steps.

Five membranes were prepared M_1, M_2, M_3, M_4, M_5, at same concentration, and different percentage of the mixture of PET-PEG (The added quantity of PEG is the same subtracted from the PET). In this work, the effect of PEG polymer of the prepared membranes on heat resistance and water vapor permeability were studied for water vapor transport applications.

III.2 Membranes fabrication:

III.2.1 Recovery of recycled PET:

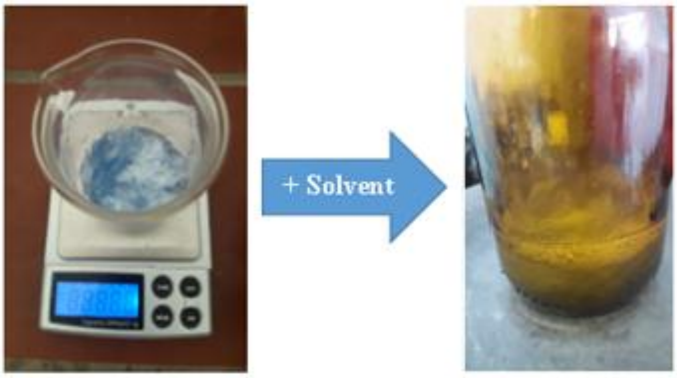
In Algeria, many brands of mineral water are sold in plastic bottles. Their polymeric family code marked on the bottles is checked, all of them were made from PET.

Firstly, water plastic bottles were segregated from other plastic bottles and were used in this experiment part for recovering of PET polymer. It were cut into small pieces of 5x5 mm², cleaned up and rinsed for 2 hours with distilled water, after drynig at Lab ambient temperature, the recycled PET polymer pieces are stocked in a glass bottle, and used for the preparation of PET membranes (**figure III-1**).

Figure III-1: Recovering of recycled PET polymer from Lalla Khedija bottles

III.2.2 Preparation of PET-Membranes casting solutions

Initially, recycled PET and solvent were placed in a glass flask and well mixed by a magnetic stirrer at room temperature until the recycled PET polymer was completely dissolved and obtained a homogenous solution (**see figure III-2**).



PET Stirring of solution

Figure III-2: Dissolving of PET in the solvent

After dissolving PET in the solvent, PEG is added to PET homogenous solution and kept under stirring to obtain a homogeneous casting solution (**figure III-3**).

PEG Casting solution

Figure III-3: Addition of PEG to PET-Solvent solution to obtain a casting solution

After formation of a homogeneous solution, the solution was hold at the ambient temperature to remove the air bubbles.

Remark:

- M_1 doesn’t contain only PET. The same difference of PEG quantity was added to the M2, M3, M4, and M5 membranes.
- The agitation of PET in solvent was kept for 24h to ensure that all PET polymer pieces are totally dissolved, and more we add PEG, more it needs more time to dissolve in the solution (see **table III-1**).

Table III-1: Agitation periods for preparation of casting solution

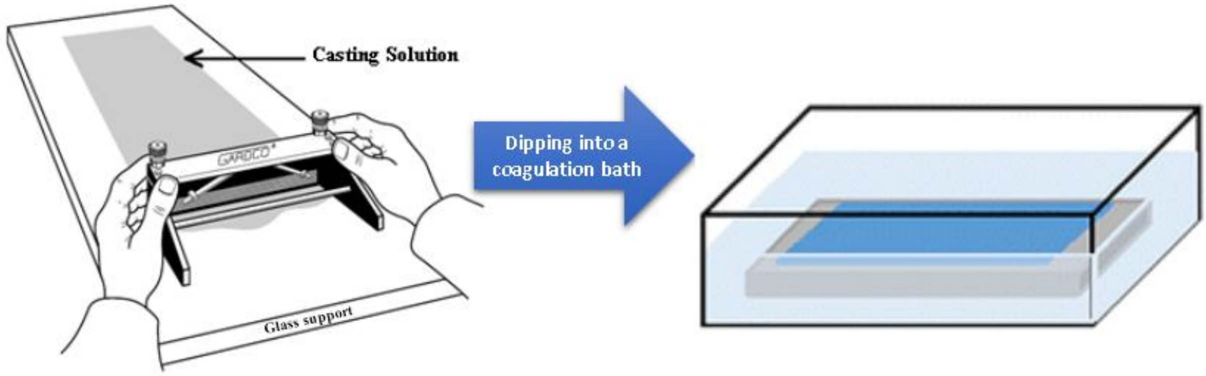
Agitation period (min)	M1	M2	M3	M4	M5
PET + Solvent	24 hours				
PEG + Solution		90	120	150	180

III.2.3 Preparation of membrane sheets

Polymer PET/PEG blend membranes were fabricated by dry/wet phase inversion process.

After disappearing of air bubbles, the prepared dope solution was cast manually on plat glass using a home glass film applicator at the room temperature with a gap clearance of 100 µm, then it was immersed into a distilled water (non-solvent) coagulation bath at ambient temperature for at least 24 h for removing almost of the solvent and water-soluble polymer (see **figure III-4**).

The formed membrane was then moved into support paper for drying.



Casting of the membrane solution

Precipitation (formation) of membrane sheet

Figure III-4: Fabrication process of all membrane sheets

III.3 Test of heat resistance

Basically, PET and PEG polymers are thermally stables, they have high melting temperatures 250°C, 160°C respectively. In this experience, it is supposed to have high resistance of prepared membranes M1, M2, M3, M4, M5 at least the resistance of melting temperature of polymers 250°-160°C.

To investigate on heat resistance of prepared membranes, the flat sheets of membranes were cut into circles with same diameter of 3,2 cm (see **figure III-5**), then put it into an oven on a glass support, the oven was equipped by temperature controller of range 0-100°C.

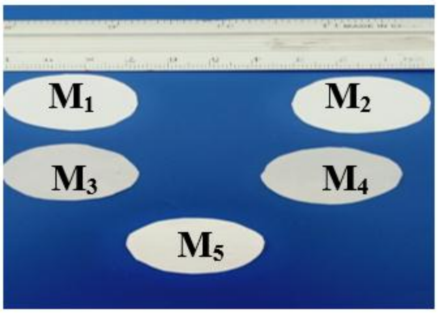


Figure III-5: Prepared membrane sheets for heat resistance

III.4 Test of water vapor transmission and permeability

Two methods are usually used for measuring water vapor trasmission rates and permeability:

- The cup of water
- The dynamic moisture permeation cell (DMPC)

In this work, the cup of water was used. The membrane sheets were cut in circles forms equal to the surface of the cup-water mouth opening. 20 ml of water was added in the cup, covered by the circular sheet of the membrane. The full load was weighted, then it was put into the oven, checked and weighted every two hours. In the controlled furnace the relative humidity and temperature were maintained at 38 °C and 10% respectively, their values were recorded during weighting of water cup. For accuracy data, weight loss was repeated 3 times for each membrane. The results are in the tables (Appendix).

The thickness of each membrane sheet was measured before and after the test by a certified digital caliper device 0-25 mm, resolution 0.001 mm.

The water vapor transmission rate (WVTR), permeance and water vapor permeability (WVP) were determined using the equations (1), (2) and (3).

III.4.1 Water vapor transmission rate (WVTR):

The water vapour transmission rate (WVTR) is the rate of water vapour permeating (flux) through the membrane film[43]:

$$\mathbf{WVTR} = \frac{\mathbf{G}}{\mathbf{t \times A}} = \frac{\mathbf{Flux}}{\mathbf{Area}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(\mathbf{1})$$

III.4.2 Permeance:

$$\mathbf{P} = \frac{\mathbf{WVTR}}{\mathbf{\Delta p}} = \frac{\mathbf{WVTR}}{\mathbf{S\,(R1 - R2)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(\mathbf{2})$$

At 38 °C, the saturation water vapor pressure is 46 mmHg (6254.436 Pa).

III.4.3 Permeability

$$\mathbf{WVP} = \mathbf{Permeance} \times \boldsymbol{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (\mathbf{3})$$

III.5 Results and discussion

III.5.1 Preparation of membrane sheets

III.5.1.1 M1 membrane:

Voids of 3-5 mm are formed in first trial of membrane sheet M1-1 fabrication.

By dry cleaning of the glass support surface, this defect was disappeared; it is observed that any disposal of particles debris on glass while casting of membrane dope solution, it would lead to form voids (see the **figure III-6**). This is explained by micro scale of membrane thickness.

During membrane formation process in the coagulation bath, the disposal of particles in castled solution in this range would form an obstacle in the membrane and a void would appear as consequence.

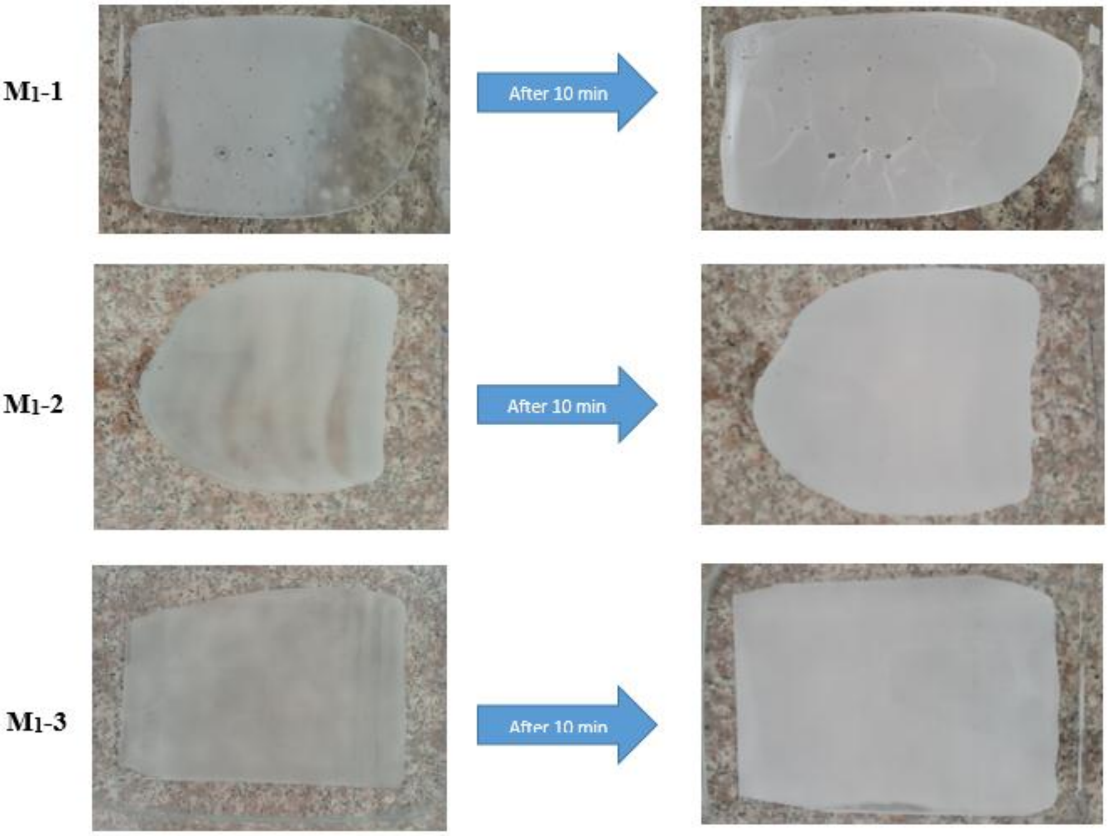


Figure III-6: Formation of membrane films M_1 in coagulation bath

III.5.1.2 M2 membrane:

The membrane sheets were well formed (**figure III-7**) almost at the same time (8 minutes).

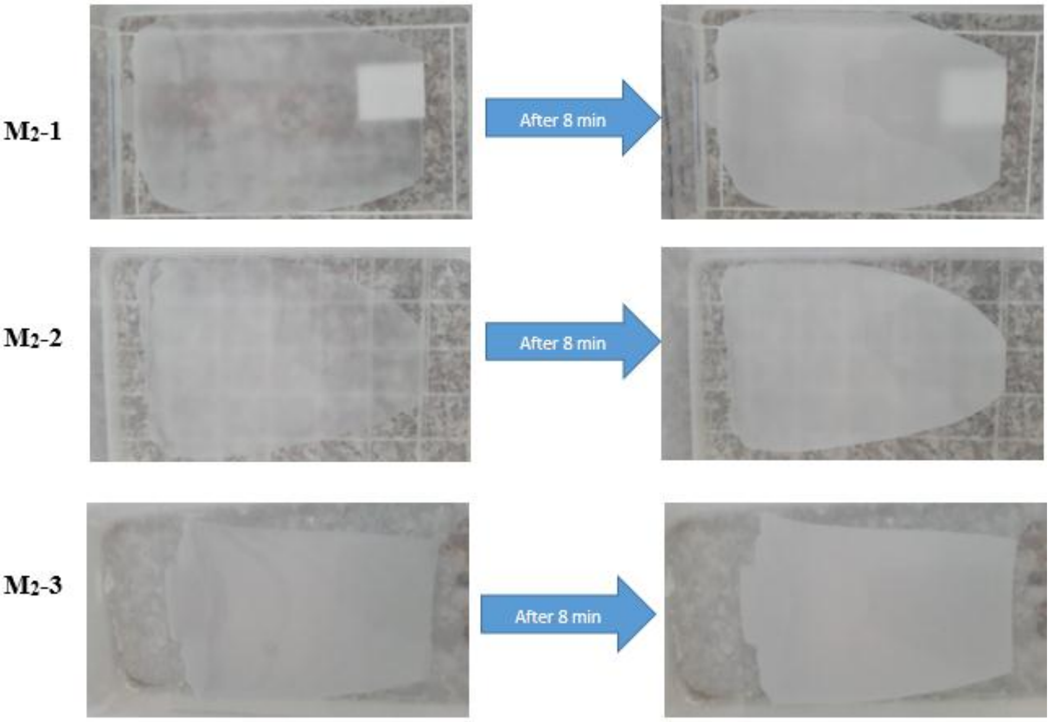


Figure III-7: Formation of membrane films M_2 in coagulation bath

III.5.1.3 M3 membrane:

The membrane sheets were well formed (**figure III-8**) almost at the same time (8 minutes).

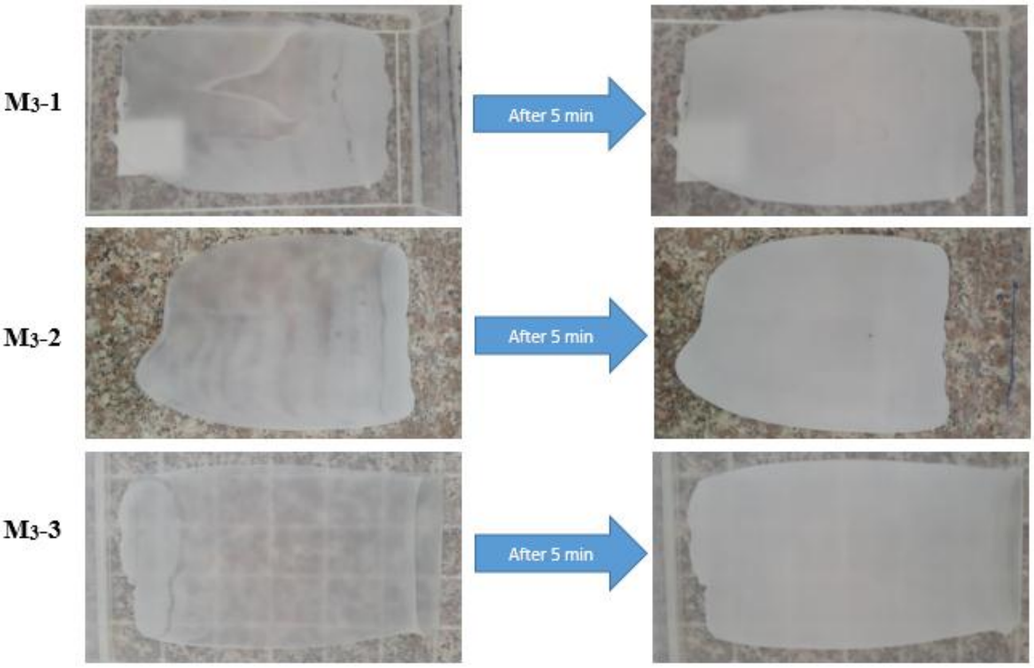


Figure III-8: Formation of membrane films M_3 in coaglutaion bath

III.5.1.4 M4 membranes:

The membrane sheets took 6 min (more than M3) to be formed, because the low room temperature(see **figure III-9**). And small macro voids are formed of 1 mm; this is explained by high percentage of PEG polymer in the prepared casting membrane solution M4.

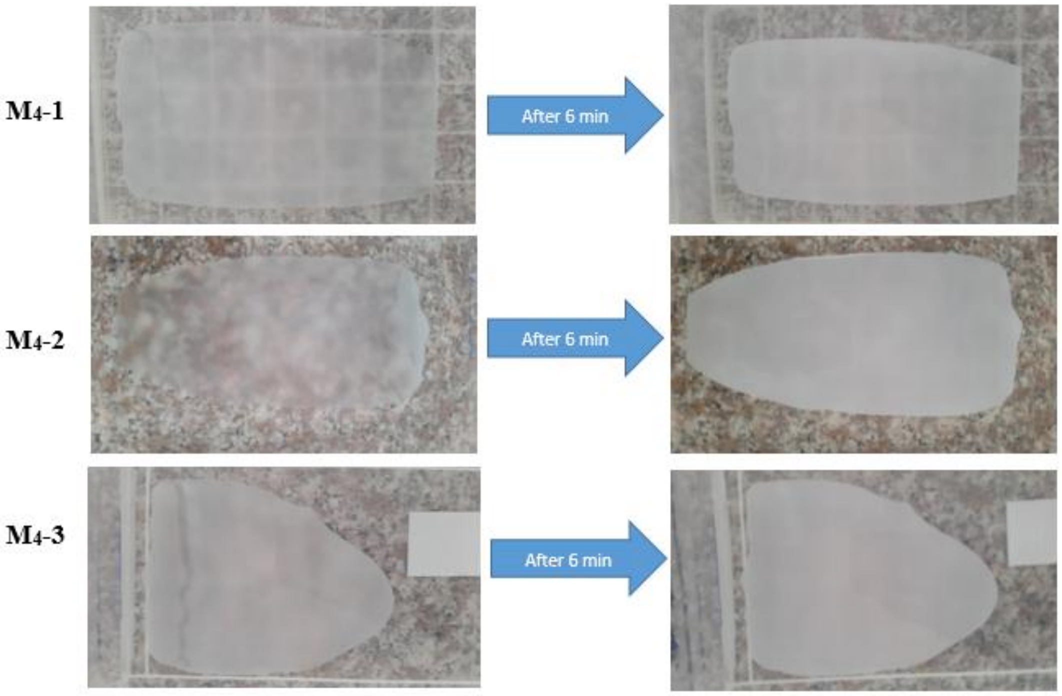


Figure III-9: Formation of membrane films M_4 in coagulation bath

III.5.1.5 M5 membrane:

After dipping the membrane films in coagulation bath, voids were appeared in membrane surfaces (**figure III-10**), this is explained by the vey high percentage of PEG in prepared casting membrane solution M5. The diameters of formed voids are in the range of 1-9 mm.

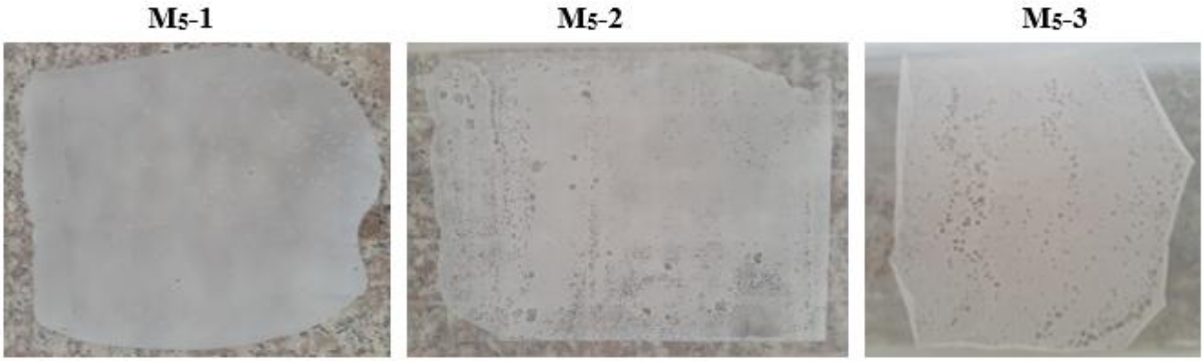


Figure III-10: Formation of membrane films M_5 in coagulation bath

Conclusion: If the percentage of PEG is high in the casting membrane solution, while the castled solution is immerged into distilled water of the coagulation bath, PEG would left the castled solution and dissolved in water, which would make voids as consequence.

III.5.2 Initial thickness measurements

The thickness (µm) was measured at different points of each flat sheet membrane. All data were captured in the table below:

Table III-2: Measurement of membrane thickness

Membrane	Thickness (µm)	Average thickness	Membrane	Thickness (µm)	Average thickness
M_1-1	100	100	**M_3-1**	74	74
M_1-2	101		**M_3-2**	74	
M_1-3	100		**M_3-3**	75	
M_2-1	85	84	**M_4-1**	60	59
M_2-2	83		**M_4-2**	60	
M_2-3	84		**M_4-3**	58	

M1 thickness of castled solution on the glass was 100 µm. After coagulation in distilled water, M1 thickness was not changed, otherwise, M2, M3, and M4, after the coagulation, the thickness was reduced to 84, 75, 59 µm respectively. This can be explained by the fact that the percentage of PEG in casting leads to systematically reduced membrane thickness. Results showed that with increase in PEG percentage, membranes will have significant decrease in thickness (**figure III-11**) **.**

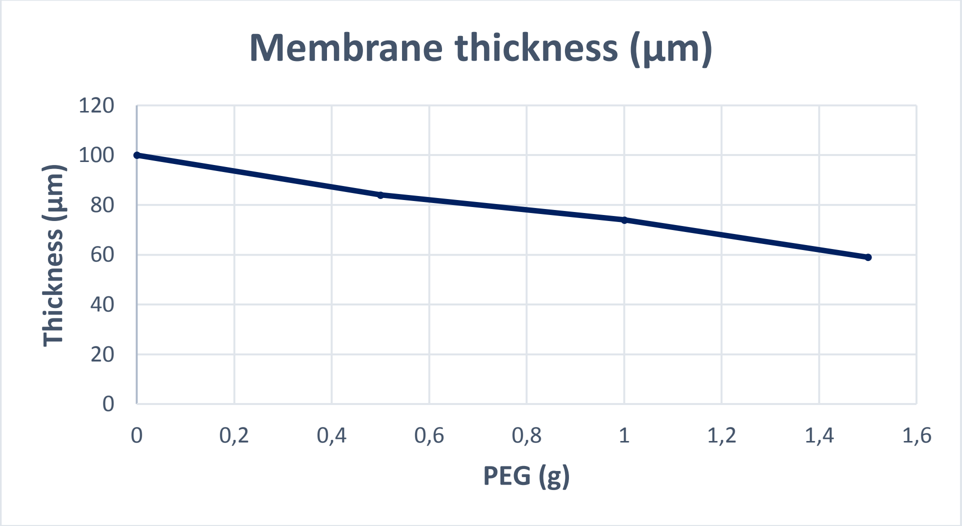


Figure III-11: PEG percentage effects on Membranes average thickness

III.5.3 Test of heat resistance

At 40°C: No change of all membranes shapes is observed.

At 50°C: No change of membranes shape of M1 to M5 is observed.

At 60°C: A slight deformation of the membrane M5, others kept their shapes.

At 70°C: Membranes M1 and M4 start to bend from edges as shown in figure below.

At 80°C: The membranes M1 and M4 are bended more and more.

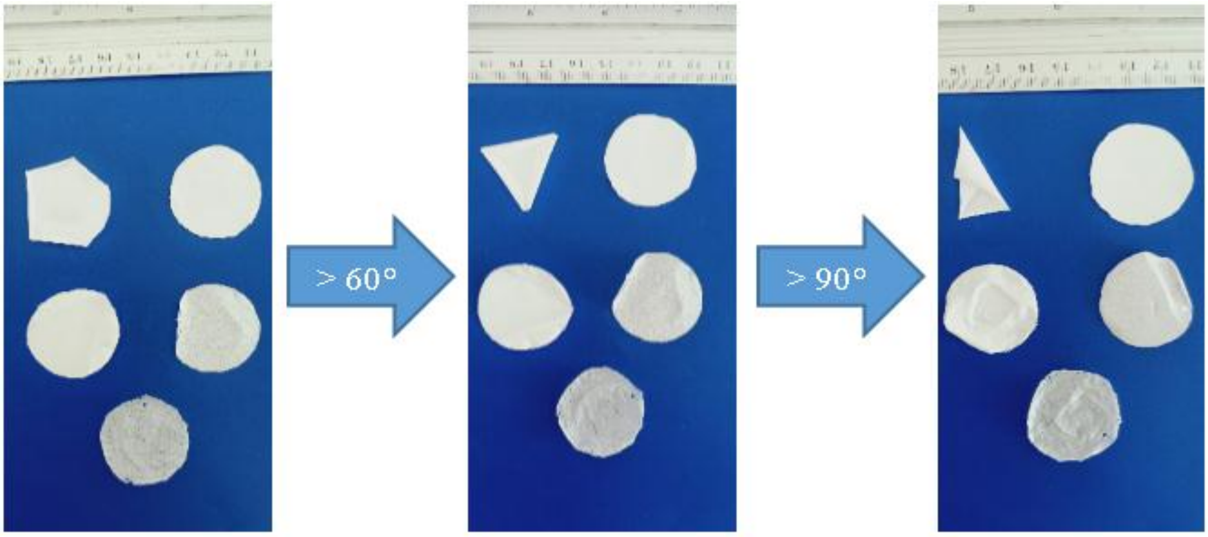


Figure III-12: The effect of temperature on membrane morphology

The evolution of the modification is presented in the table below.

Table III-3: Test of heat resistance

T°	**Observations**			
	M1	**M2**	**M3**	**M4**
40-50	Shapes not changed	Shapes not changed but it stucks on the glass	Shape not changed.	no change
50-60				
6+0-70	≥ 60°C, Change of the shape, bend of the membrane		≥ 70°C Signs of Melting.	≥ 70°C Change of the shape, bend of the membrane
70-80				
80-90				

The resistance of M1 was poor, bending started at temperature at 60. By adding PEG polymer, the heat resistance is improved M3, M4 bend at 70C, No deformation for M2.

Conclusion : Based on resistance data results, the membrane M2 shows higher resistance compared to other membranes. M3 and M4 have better resistance compared to membrane M1.

III.5.4 Test of water vapor transmission rate and permeability

III.5.4.1 Calculate the water vapor transmission WVTR (g.d^{-1}.m^{-2}):

It was determined from the slope of the regression line of weight variation versus time (flux) graph (**Table III-4**), whereby the slope is then divided by the area of the film being exposed to the transmission (**Table III-5**).

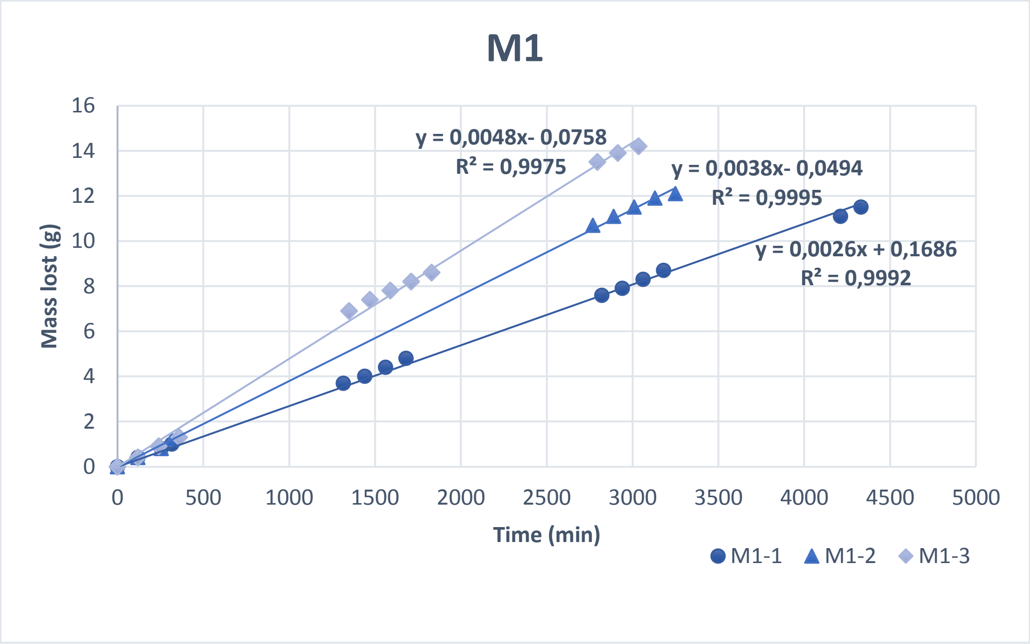


Figure III-13: The water mass loss of M1 versus time

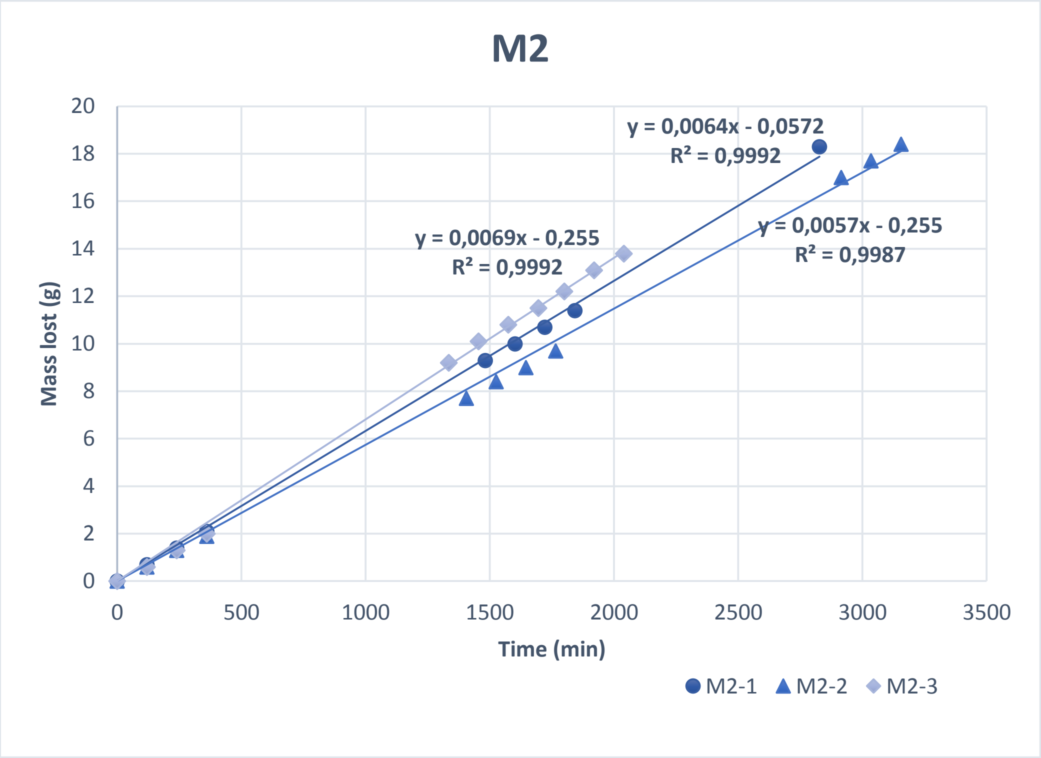


Figure III-14: The water mass loss of M2 versus time

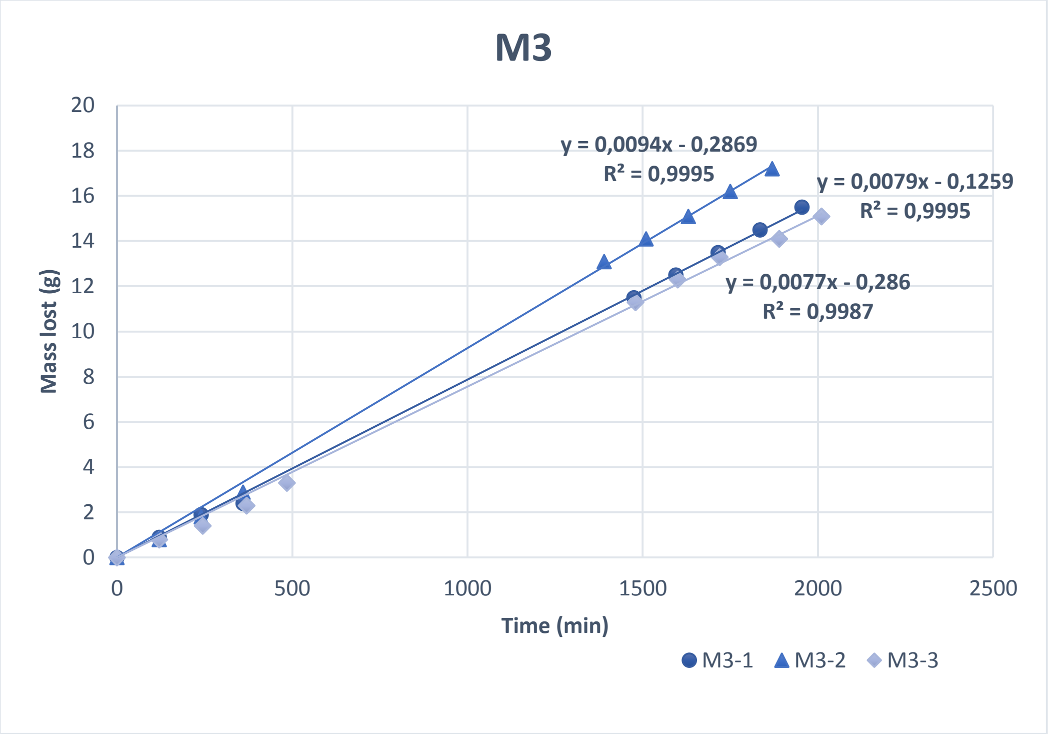


Figure III-15: The water mass loss of M3 versus time

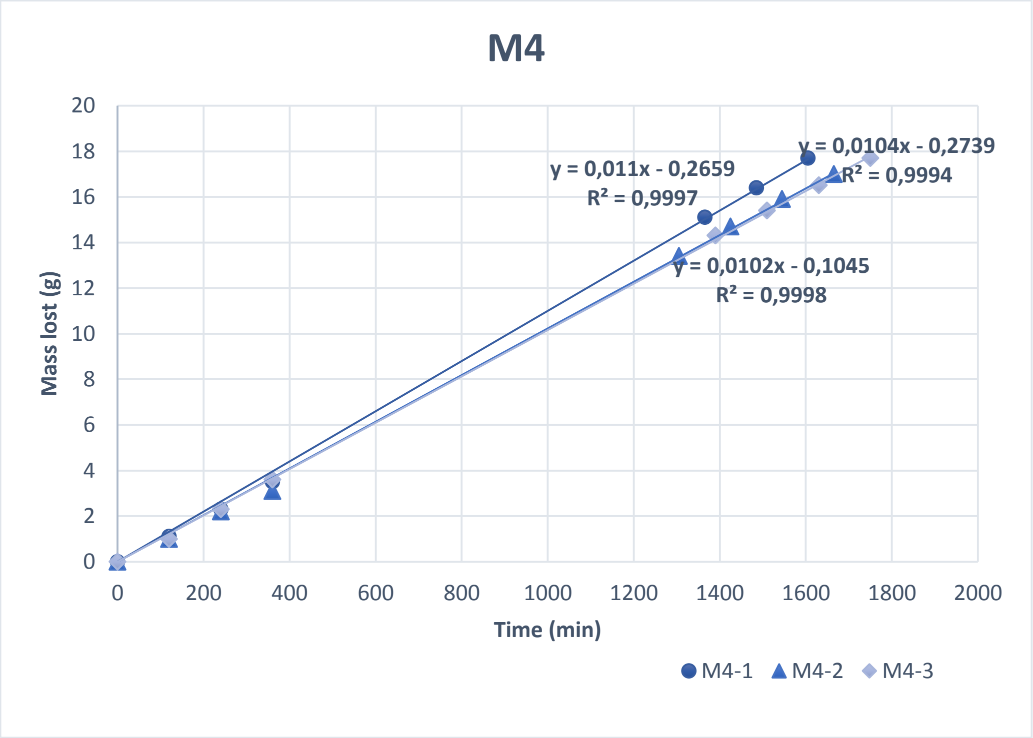


Figure III-16: The water mass loss of M4 versus time

All membranes regression lines are drawn using the values of mass lost during time in the tables at appendix.

Table III-4: Average slopes (flux) of membranes weight variation regression lines

Membrane	slope α_1	slope α_2	slope α_3	Average flux
M1	0,0048	0,0038	0,0026	**0,003733**
M2	0,0069	0,0064	0,0057	**0,006267**
M3	0,0079	0,0094	0,0077	**0,008333**
M4	0,0112	0,0104	0,0102	**0,010600**

$$WVTR = \frac{Mass\ H2O\ loss}{Time * aera} = \frac{Flux}{Area}$$; Area of cup water = 0,003019 m2

Table III-5: Water vapor transmission (WVTR) of membrane per day

Membrane	Flux H_2O (g/min)	WVTR ($g.min^{-1}.m^{-2}$)	WVTR ($g.d^{-1}.m^{-2}$)
M1	0,003	1,2365	**1780,563**
M2	0,006	2,07585	**2989,228**
M3	0,008	2,76019	**3974,667**
M4	0,010	3,5111	**5055,979**

III.5.4.2 Membranes permeance

$$P = \frac{WVTR}{\Delta p} = \frac{WVTR}{Ps\,(R1-R2)}$$ $P_s = 6254{,}44$ Pa

Table III-6: Permeance of membranes M1, M2, M3, and M4.

Membrane	WVTR ($g.d^{-1}.m^{-2}$)	R2	*Permeance* ($g.min^{-1}m^{-2}Pa^{-1}$)
M1	**1780,563**	10	0,003
M2	**2989,228**	11	0,005
M3	**3974,667**	12	0,007
M4	**5055,979**	14	0,009

III.5.4.3 Water vapor permeability

$$WVP = P * l$$

Table III-7: Permeability of membrane per day

Membrane	P ($g.min^{-1}m^{-2}Pa^{-1}$)	Thickness, l (µm)	WVP ($g.\mu m.min^{-1}m^{-2}Pa^{-1}$)
M1	0,003	100	**0,316**
M2	0,005	84	**0,456**
M3	0,007	74	**0,534**
M4	0,009	59	**0,555**

The water vapor permeability values comparing to the additive quantity of PEG were presented in the figure below:

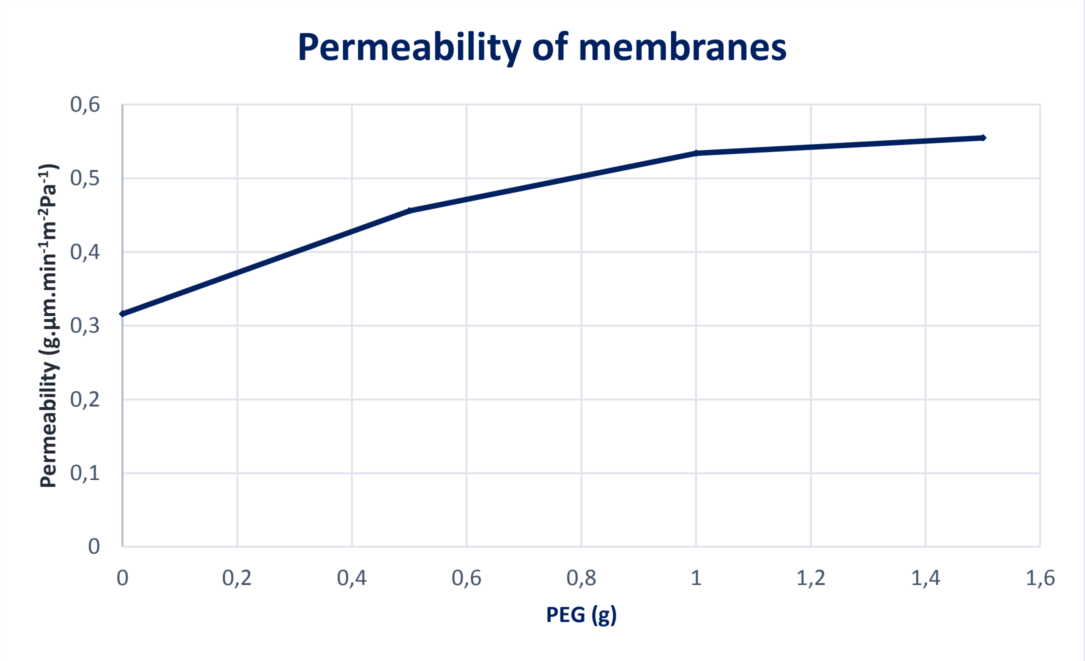


Figure III-17: The effect of PEG on permeability of membranes M1, M2, M3 and M4.

The water vapour permeability is directly proportional to the WVTR values, it is expected for the WVP values to exhibit the same trend as that of the WVTR.

In general, the water vapour permeability through the film increases with an increase of PEG addition percentage.

III.5.5 Final thickness measurement

Data in table **Table III-8** shows that membranes with low PEG percentage provide a higher resistance effect on water vapour permeance, this results in continuous force pushing the membrane film sheet during the cup of water test. That leads in membrane elongation where the initial thickness is loosed (decreased).

Table III-8: Effect of PEG (%) on thickness loss in cup of water

Thickness (µm)	**M1**	**M2**	**M3**	**M4**
Before	100	85	75	60
after	68	60	55	42
Δ*l* (µm)	33	25	20	18

The figure below shows that more PEG increases, more the difference of thickness before and after permeation test decrease.

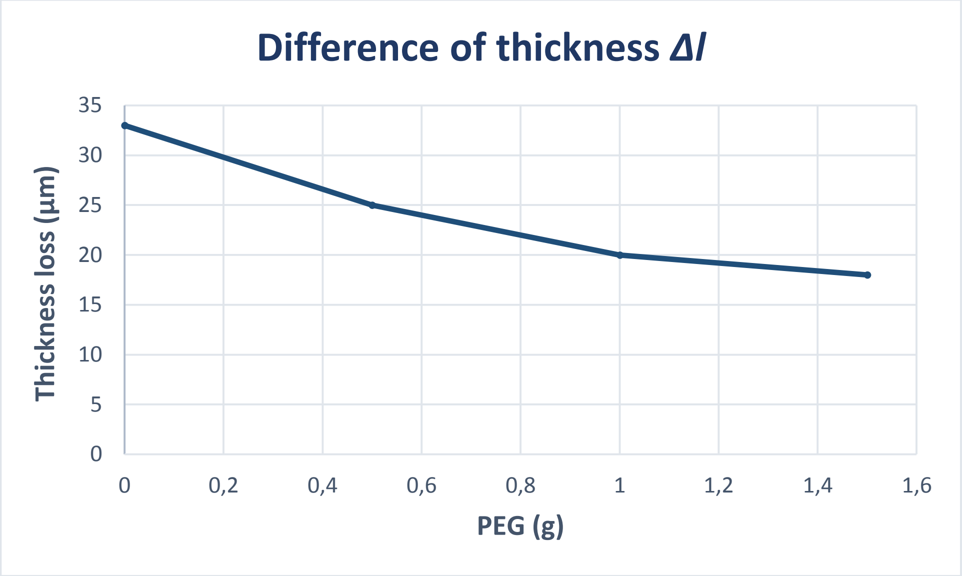


Figure III-18: Effect of PEG on thickness decrease in cup-water

Conclusion

In 2017, nearly 328,343 tons of PET plastic was recovered from waste discharge of Mostaganem. After only one year, in 2018, the quantity is doubled to twice 613,635 tons. This significant increase of PET plastic making an alert for any failure of plastic reuse which ends up plastic dispersed in the environment.

So, a successful potential solution where made in this study which could recycle plastic and breaking down waste PET plastic. It relies on using of PET plastic to make PET membranes for water vapor transport applications purpose.

The phase inversion technique was used for preparation of PET membranes of recycled plastic bottles, and their morphology and permeability were improved by the addition of PEG polymer.

The prepared membranes are used for vapor transport applications, they can be used for: Gas dehydration, water vapor removal from natural gas, from methane, from LPG, from bio methane. They could be used as humidifiers.

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Appendix

Table 1: Mass lost (g) of M_1 versus time (min)

M_1-1		M_1-2		M_1-3	
Time	**Mass lost**	**Time**	**Mass lost**	**Time**	**Mass lost**
0	0	0	0	0	0
120	0,4	120	0,4	120	0,4
256	0,8	256	0,8	240	0,9
316	1	316	1,2	360	1,3
1316	3,7	2770	10,7	1350	6,9
1441	4	2890	11,1	1470	7,4
1561	4,4	3010	11,5	1590	7,8
1681	4,8	3130	11,9	1710	8,2
2821	7,6	3250	12,1	1830	8,6
2941	7,9			2795	13,5
3061	8,3			2915	13,9
3181	8,7			3035	14,2
4211	11,1				
4331	11,5				

Table 2: Mass lost (g) of M_2 versus time (min)

M_2-1		M_2-2		M_2-3	
Time	**Mass lost**	**Time**	**Mass lost**	**Time**	**Mass lost**
0	0	0	0	0	0
120	0,7	120	0,6	120	0,6
240	1,4	240	1,3	240	1,3
360	2,1	360	1,9	360	2
1482	9,3	1405	7,7	1335	9,2
1602	10	1525	8,4	1455	10,1
1722	10,7	1645	9	1575	10,8
1842	11,4	1765	9,7	1695	11,5
2827	18,3	2915	17	1800	12,2
2947	19	3035	17,7	1920	13,1
3067	19,7	3155	18,4	2040	13,8

Table 3: Mass lost (g) of M_3 versus time (min)

M_3-1		M_3-2		M_3-3	
Time	**Mass lost**	**Time**	**Mass lost**	**Time**	**Mass lost**
0	0	0	0	0	0
120	0,9	120	0,8	120	0,8
240	1,9	240	1,8	245	1,4
360	2,4	360	2,9	370	2,3
1475	11,5	1390	13,1	485	3,3
1595	12,5	1510	14,1	1480	11,3
1715	13,5	1630	15,1	1600	12,3
1835	14,5	1750	16,2	1720	13,3
1955	15,5	1870	17,2	1890	14,1

Table 4: Mass lost (g) of M_4 versus time (min)

M_4-1		**M_4-2**		**M_4-3**	
Time	**Mass lost**	**Time**	**Mass lost**	**Time**	**Mass lost**
0	0	0	0	0	0
120	1,1	120	1	120	1
240	2,3	240	2,2	240	2,3
360	3,5	360	3,1	360	3,6
1365	15,1	1305	13,4	1390	14,3
1485	16,4	1425	14,7	1510	15,4
1605	17,7	1545	15,9	1630	16,5
1725	19	1665	17	1750	17,7