Preparation of Polyamide Membranes and Studies There Chemical, Physical and Mechanical Properties and Its Application

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Abstract: As known, a huge part of all commercially available membranes prepared by immersion precipitation. This way is a primary way to get flat membranes. The advantages of immersion precipitation are wide field of the polymers, which can be used.

In the experimental part of this work, fourmembrane samples were made with different casting parameters (polymer concentration in the casting solution and evaporation time of solvent)were tested for chemical properties(chlorine tolerance and PH rang) and physical properties (pore size and porosity) and mechanical properties (viscosity, tensile strength and strain).

The results showed that PA (25%) membrane having the higher (chlorine tolerance, PH rang, viscosity, tensile strength, and strain) but it was having the lowest (pore size and porosity).

In addition, we have determination of poly ABS molecular weight by knownits osmotic pressure.

Keywords: membrane, polyamide, immersion precipitation, chemical, physical, mechanical properties, osmotic pressure.

Introduction

By far the most of the technically used membranes made from polymers and via phase inversion method. The concept of phase inversion covers a range of different techniques to processing a film of a polymer solution into a porous membrane such as:

- Thermally Induced Phase Separation (**TIPS**)

  : Precipitation by cooling.

- Non solvent Induced Phase Separation (**NIPS**)

  : Immersion Precipitation in a non-solvent (typically water).

- Vapor Induced Phase Separation (**VIPS**)

  : Precipitation by absorption of non-solvent (water) from the vapor phase.

- Evaporation Induced Phase Separation (**EIPS**)

  : Dry Casting-solvent evaporation[10, 3].

The mechanism of phase inversion is a determinant factor in the membranes morphology. The conditions for the membranes preparation (polymer concentration, type of solvent, time and temperature of casting and composition of coagulation bath) may directly influence their morphology and transport properties.

Aliphatic polyamide, such as nylon 66 have been employed for manufacturing porous membranes by nonsolvent induced phase separation (**NIPS**) immersion precipitation that depends on casting polymer solution (polymer + solvent) on a suitable support and immersed in a coagulation bath containing a nonsolvent(water). Precipitation occurs because of the exchange of solvent and nonsolvent. The membrane structure ultimately obtained results from a combination of mass transfer and phase separation[3].

In this article we preparation different concentration of polymeric solution, then chose the free defect PA membrane, and studies their properties.

For chemical properties of membrane, aqueous sodium hypochlorite solution (NaOCL) used for chlorine tolerance[12], HCL solution and NaOH solution used to determination of PH rang[13].

For physical properties of membrane, isobutanol solution used for membrane porosity[14], bubble point test used to determination of membrane pore size[15, 16].

For mechanical properties of membrane, UBBELOHDE viscometer used to determination of [K_{wert}-Value, intrinsic viscosity [η] and molecular weight for the studied polymers][17], tensile test machine used to determination of tensile strength and strain[18,19].

For determination of poly ABS molecular weight, we used osmometer instrument to knowing its osmotic pressure.

Experimental

Materials and device

Polyamide 66, formic acid (d=1.22 g/cm^3), sodium hypochlorite solution (NaOCL) (d=1.25 g/cm^3, 14%), HCL solution, NaOH solution, isobutanol solution (d=0.8 g/cm^3), sodium metabisulfite solution ($Na_2S_2O_5$ 1%), poly ABS (d=1.04 g/cm^3), UBBELOHDE viscometer, tensile test machine.

Membrane Preparation

Different polymer solution prepared by dissolving polyamide in formic acid to achieve homogenous solutions casting at room temperature (± 25°C) on glass plate by casting stainless steel knife. The solvent evaporated partially from the casting solution (evaporation time stage of solvent differ depends on concentration of polymer solution listed in Table 1), then the glass plate immersed in a coagulation bath containing deionized water. Immediately after the contact with water, a variation in film color occurs from clear to white, followed by the detachment of the film from the glass plate surface. After polymer coagulation, the prepared membranes transfer to a second bath containing fresh distilled water to remove any residual solvent, then the produced membrane saved in sodium metabisulfite solution ($Na_2S_2O_5$ 1%) in a cool dark place[1,2,4,5,6,7,8,9,11].

Table 1: Relationshipbetween evaporation time of solvent and of PA solution concentration.

25%	20%	15%	12%	**Concentration of PA solution %(w/v)**
1	1.30	2.15	3	**Evaporation Time (hour)**

Chemical properties of membrane

❖ Chlorine Tolerance

Membrane samples immersed for 24 h in different aqueous solution chlorine (2000, 3000, 4000 ppm CL⁻) prepared from stock aqueous NaOCL solution (14%), and then compared chlorine–exposed membrane weight with dry membrane weight[12].

❖ PH Rang

Membrane samples immersed for 24 h in solution with changing pH from (3-10). The pH of the solutions controlled by addition of NaOH (1.0N) or HCl (1.0N) solution, and then compared PH–exposed membrane weight with dry membrane weight[13].

Physical properties of membrane

❖ Membrane porosity

Membranes samples cut into small pieces and immersed in isobutanol for 24 h. The impregnated membrane dry with tissue papers to remove the residual isobutanol on the membranes. The mass of the samples before and after immersing in isobutanol measured using a digital microbalance. The porosity of the membrane P% is defined as the pore volume divided by the total volume of the membrane as follow in equation 1:

$$P\% = \frac{(w_w - w_d) \times \rho_p}{(w_w - w_d) \times \rho_p + w_d \times \rho_i} \times 100\%$$ (1)

w_w: mass of wet membrane with isobutanol (g).

w_d: mass of dry membrane (g).

ρ_i: isobutanol density (0.802 g/cm^3).

ρ_p: polyamide membranes density (g/cm^3)[14].

❖ Pore size

Bubble point test used to determination of pore size, this method is based on measurement of the pressure necessary to blow air through a water-filled porous membrane, an air bubble will penetrate through a pore of radius r_p when the transmembrane pressure difference $\Delta p = p_1 - p_2$ given by the following equation 2:

$$r_P = \frac{2\gamma \cos\theta}{\Delta P}$$ (2)

r = radius of the capillary (m).

γ= surface tension (water/air) (0.072 N/m).

θ= contact angle.

Δp= pressure difference across membrane (N/m^2)[15, 16].

Mechanical properties of membrane

❖ K_{wert}-Value, intrinsic viscosity and viscositymolecular weight

Relative viscosity η_{rel} and intrinsic viscosity [η] of the polymer solution are measured using UBBELOHDE viscometer by known the time of solution and solvent flux in the instrument.

The relative viscosity obtained from equation 3:

$$\eta_{rel} = \frac{t}{t_0}$$ (3)

t: flux time of polymer solution (sec).

t_0: flux time of solvent (sec).

K_{wert}-Value obtained from equation 4:

$$Log\eta_{rel} = \left(\frac{75k^2}{1+1.5 \times k \times C} + k\right)C$$ (4)

η_{rel}: relative viscosity.

C: polymer solution concentration (g/100ml).

K_{wert}-Value=1000×k

The intrinsic viscosity obtained from equation 5:

$$[\eta] = \frac{0.25(\eta_{rel} - 1) + (1.725 \, Log \eta_{rel})}{C} \tag{5}$$

Viscosity average molecular weight M_v of the studied polymer calculated by using Mrak-Houwink equation 6:

$$[\eta] = K.M_v^{\alpha} \tag{6}$$

Where K and α are constant[17].

❖ Tensile strength and strain

Tensile test machine used for determination tensile strength and strain, the machine applied a force to the specimen.

Tensile stress (σ)(Kg/cm^2)is a ratio of tensile load (F) at break applied to the specimen to its original cross-sectional area (S)[before any load applied] as shown in equation 7:

$$\sigma = \frac{F}{S} \tag{7}$$

F: applied force to specimen cross section (Kg).

S: specimen area (cm^2) = $b_{specimen\ width\ (cm)}$*$\delta_{specimen\ thickness\ (cm)}$

Strain (ε) is a ratio of increases specimen gauge length ΔL at rupture to its original gauge length L_0 as shown in equation 8:

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0} \tag{8}$$

L_0: original length before any load applied (=1.2 cm).

L: instantaneous length (cm).

Young's Modulus (Modulus of Elasticity) (E) (Kg/cm^2) is a constant of proportionality between stress (σ) and strain (ε) as shown in equation 9:[18,19]

$$E = \sigma/\varepsilon \tag{9}$$

Membrane application

To determination of poly ABS molecular weight, we used prepared PA membranes (as semipermeable membrane) in osmometer instrument to know its osmotic pressure. The osmotic pressure is the pressure exerted by the column of a solution of height h that shown in equation 10:

$$\pi = \rho.g.h \tag{10}$$

ρ: density of polymer solution (g/cm^3).

g: gravity (9.8 m/s^2).

h: high of solution in instrument column (cm).

After know the osmotic pressure of polymer solution, we used relationship among the pressure, temperature, and molarity described by simple proportionalities summarized by the ideal gas equation to obtain the molecular weight (M_n) of polymer that shown in the following equation 11:

$$\pi = c.R.T = c_1.R.T/M_n$$ **(11)**

c: polymer solution concentration (mol/l).

c_1: polymer solution concentration (g/1000 ml).

R: ideal gas constant= 0.082 (atm/mol.K).

T: temperature (K^0).
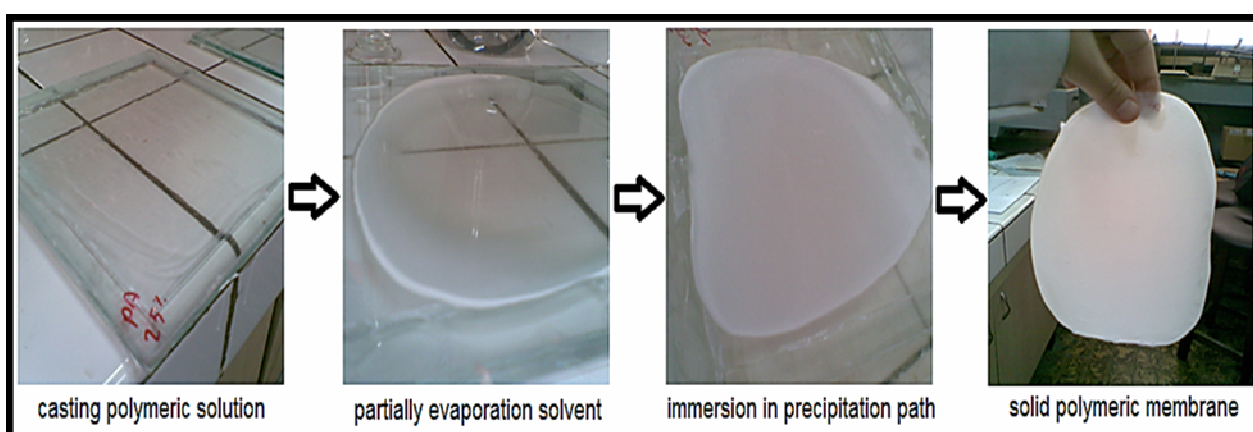
Results and Discussion

Membrane preparation

Polymeric solutions of PA prepared with different concentration, chose the perfect membrane based on free defect (holes) and have acceptable thickness. The prepared membranes shown in Table 2:

Table 2: Relationship between polymer solution concentration and prepared membrane.

Polymer solution concentration% (w/v)	Prepared membrane	Result
From 1% to 10%	Top-layer with defects (gaps, bubbles), weak and extremely thin	Bad for membrane formation
12% and 15%	Top-layer without any visible defects, thin (0.09-0.12 mm)	Good for membrane formation
20% and 25%	Top-layer without any visible defects, thick (0.15-0.19 mm)	Good for membrane formation
➢ 25%	Very difficult to polymer solved in solvent	-

As followed in Table 2, the perfect polymer solutions concentrationto prepared membrane are (12%-15%-20%-25%) with free defect top-layer.

Figure 1 show membrane casting steps:

casting polymeric solution   partially evaporation solvent   immersion in precipitation path   solid polymeric membrane

Figure 1: **Membrane casting steps**

Chlorine tolerance and PH rang membrane

Four membrane prepared PA (12%-15%-20%-25%) tested for chlorine tolerance and PH range, the experimental showed that higher chlorine tolerance and higher PH range was for PA (20%-25%) membrane as shown in Table 3:

Table 3: Chlorine tolerance and PH rang for prepared membrane

PA membrane	Chlorine tolerance (ppm CL⁻)	PH rang
PA 12%	1000	5-9
PA 15%	2000	5-9
PA 20%	3000	3-10
PA 25%	3000	3-10

Membrane porosity and pore size

Four membrane tested for porosity, result show that when the membrane thickness increase, the porosity will be decrease and the pore membrane size will be smaller, that described in Table 4:

Table 4: Porosity and pore size for prepared membrane.

PA membrane	Porosity %	Pore size (μm)
PA 12%	80	1.2
PA 15%	75	0.65
PA 20%	73	0.22
PA 25%	68	0.1

K_{wert}-Value, intrinsic viscosity and viscosity molecular weight

Relative viscosity η_{rel} of the polymer solutions are measured using UBBELOHDE viscometer by known the time of solution and solvent flux in the instrument by using equation (3).

Then determination of K_{wert}-Value by using equation (4) by using polymer solution concentration, where K_{wert}-Value is a constant characterization each polymer and it does not depends on concentration.

Then determination ofintrinsic viscosity by using equation (5), then determination of viscosity molecular weight by using equation (6), they are described in Figure 2.
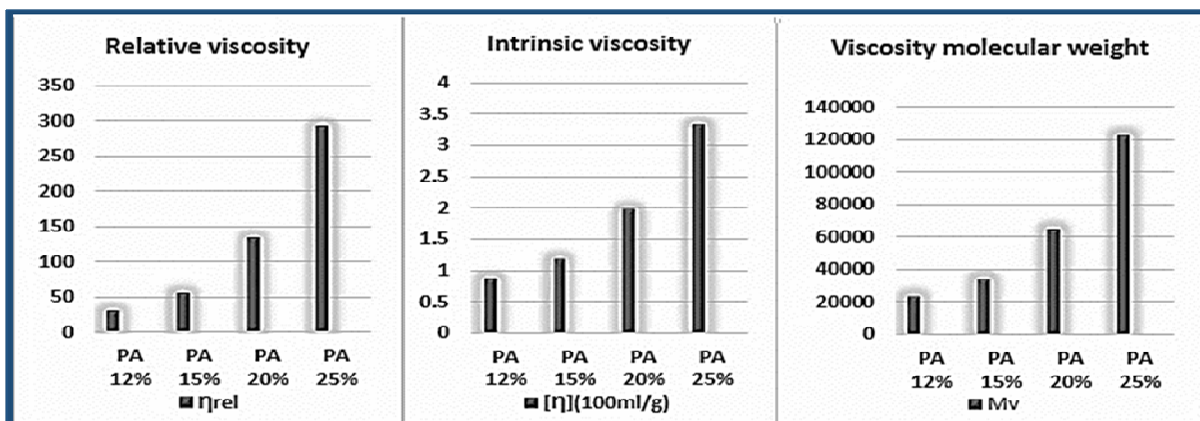
Where: α=0.82

k =0.000226 (100ml/g)

K_{wert}-Value =1000×k

$t_{0(formic\ acid)}$ = 11.87 (sec)

We obtained that K_{wert}-Value (PA) = 44.5

Figure 2 : Relative viscosity,intrinsic viscosity and viscosity molecular weight for prepared PA solutions

As shown in Figure 2, every relative viscosity, intrinsic viscosity and viscosity molecular weight increased by increasing of polymer solution concentration.
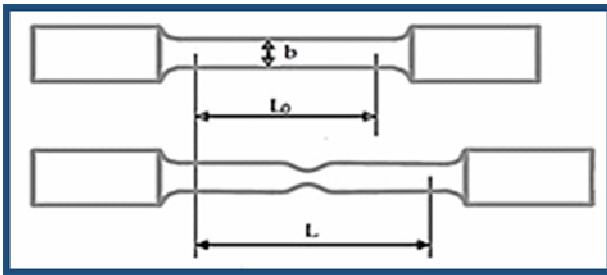
Tensile strength, Strain and Young's Modulus

Tensile test machine used for determination of tensile strength, strain and Young's Modulus, that obtained from equation (7) (8) (9).

Where:

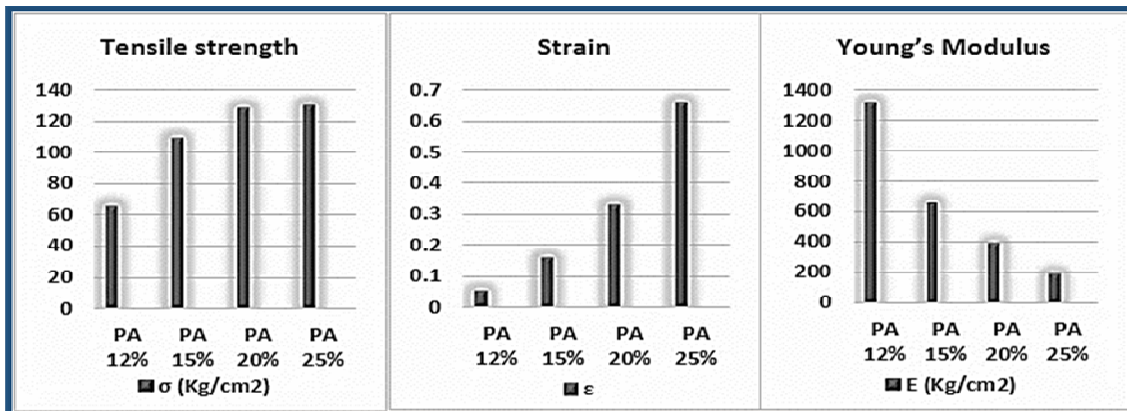L_0: original length before any load is applied (=1.2 cm).

b: specimen width (=0.8 cm).

As shown in Figure 3:

Figure 3: **Standerd tensile test specimen**

The result shown, PA (25%) membrane have the higher tensile strength and strain compared with other membrane, but it's have the lowest Young's Modulus (stiffness) that shown in Figure 4:

Figure 4*: **Tensile strength, Strain and Young's Modulus for prepared membrane**

Poly ABS molecular weight

To determination of poly ABS molecular weight, prepared of poly ABS solution (9g/100ml).

The result show, the height h in the osmometer instrument was:

h=0.22 cm

By using equation 10: the osmotic pressure for poly ABS solution is:

$$\pi = \rho.g.h \qquad \textbf{(10)}$$

Where: density (ABS 9%) =1.47 g/cm^3.

The osmotic pressure for poly ABS solution is π= 326 (dyn/cm^2).

By using equation 11:

$$\pi = c_1.R.T/M_n \qquad \textbf{(11)}$$

Where:

$c_1 = 90$ (g/1000 ml)

R: 0.082 (atm/mol.K)

T: 298 (K^0)

The molecular weight of polymer ABS is M_n= 6834 (mol/g)

Conclusions

The result show in this article:

- ❖ The suitable polymer solutions concentration for prepared membrane are (12%-15%-20%-25%) with free defect top-layer.
- ❖ The higher chlorine tolerance and PH range was for PA (20%-25%) membrane.
- ❖ When membrane thickness increase, porosity will be decrease and the pore membrane size will be smaller.
- ❖ Relative viscosity, intrinsic viscosity and viscosity molecular weight increased by increasing of polymer solution concentration.
- ❖ PA (25%) membrane have the higher tensile strength and strain compared with other membrane, but have the lowest Young's Modulus.
- ❖ Poly ABS solution (9g/100ml) molecular weight is 6834 (mol/g).

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