

Preparation of Semipermeable Polycarbonate Membranes and Study Their Chemical, Physical and Mechanical Properties and one of Its Application

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ABSTRACT

Now polycarbonate (PC) used to make semipermeable membranes by the phase inversion process, this way is a primary way to get flat membranes.

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

The results showed that PC (10%, 12%) membrane having the higher chlorine tolerance and pH rang, on the other hand membrane (PC 12%) having the higher viscosity, tensile strength and strain but it was having the lowest pore size and porosity.

One of the membrane application was the determination of average molecular weight for any polymer, so we determined the polystyrene (PS) molecular weight by knowing its osmotic pressure.

Key words: Semipermeable membrane of polycarbonate (PC), Phase inversion process, Polystyrene (PS), Osmotic pressure.

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تحضير أغشية نصف نفوذة من البولي كربونات ودراسة خواصها الكيميائية، الفيزيائية والميكانيكية وأحد تطبيقاتها العملية

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الملخص

يستخدم بوليمر البولي كربونات (PC) في صناعة أغشية نصف نفوذة باستخدام عملية تحول الحالة (phase inversion process) وتعد هذه العملية الأساس في الحصول على أغشية مستوية. في الجزء العملي من البحث، حُضرت أربعة أغشية مختلفة من حيث تركيز البوليمر في المحلول، ودرست الخواص الكيميائية (درجة تحمل الأغشية لتركيز الكلور ومجال الـ pH)، والخواص الفيزيائية (اللزوجة والمسامية وحجم ثقوب الغشاء)، والخواص الميكانيكية (قوة الشد والانفعال). أظهرت النتائج أن كلاً من غشاء البولي كربونات (10%, 12% PC) كان الأعلى من حيث درجة تحمله لتركيز الكلور ومجال الـ pH، في حين أن غشاء البولي كربونات (12% PC) كان الأعلى من حيث اللزوجة وقوة الشد والانفعال، لكنه كان الأدنى من حيث المسامية وحجم الثقوب مقارنة بالأغشية الأخرى المحضرة. ومن التطبيقات العملية للأغشية تحديد معدل الوزن الجزيئي لأي بوليمر، فحُد معدل الوزن الجزيئي لبوليمر البولي ستيرن (PS) وذلك بمعرفة ضغطه الحلوي.

الكلمات المفتاحية: غشاء نصف نفوذ من البولي كربونات، عملية تحول الحالة، بولي ستيرن، الضغط الحلوي.

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Introduction

Phase inversion technique is still the most popular and important preparation method, especially for commercial membrane production. In the process of the phase preparation of polymeric membranes, the polymer solutions precipitated by different approaches.

According to the change of the operating parameters that induce the phase inversion, two different separation mechanisms are involved:

1. **Thermally induced phase separation (TIPS):** by decreasing the temperature of the polymer solution, the precipitation is induced.
2. **Diffusion induced phase separation (DIPS):** by contacting, a polymer solution with a vapor or liquid, diffusional mass exchange leads to a change in the local composition of the polymer film and the precipitation is induced [1,2,3].

Three types of techniques developed to reach DIPS:

- a. Immersion precipitation: The casting solution is immersed into a nonsolvent bath, and the nonsolvent from the coagulation bath diffuses into the casting solution and the solvent diffuses from the casting solution into the nonsolvent bath, which causes a rapid precipitation of the casting solution from the top surface downward.
- b. Vapor adsorption: The casting solution subjected to a vapor containing nonsolvent and some gases (such as air, nitrogen, etc.). The adsorption of the nonsolvent will cause the precipitation of the casting solution.
- c. Solvent evaporation: The casting solutions are prepared with a volatile solvent, with little or without volatile nonsolvent and a polymer. Preferential evaporation of the volatile solvent will generate unstable compositions and precipitation will be induced [4,5].

The mechanism of phase inversion is a determinant factor in the membranes morphology. The conditions for the membranes

preparation (polymer concentration, type of solvent) may directly influence their morphology and transport properties.

Polycarbonate have been employed for manufacturing porous membranes by thermally induced phase separation (TIPS), that depends on casting polymer solution (polymer + solvent) on a suitable support and phase separated by lowering the temperature of the casting solution [6,7].

In this article, we prepared different concentration of polymeric solution, then chose the free defect PC membrane, and studied their properties.

For chemical properties of membrane, aqueous sodium hypochlorite solution (NaOCl) used for chlorine tolerance [12], HCl solution and NaOH solution used to determine the pH rang [13].

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

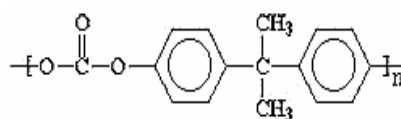
For mechanical properties of membrane, UBBELOHDE viscometer is used for the determination of [K_{wert} -Value, intrinsic viscosity $[\eta]$ and molecular weight for the studied polymers] [17], tensile test machine is used for the determination of tensile strength and strain [18,19].

For the determination of polystyrene molecular weight, we used osmometer instrument to know its osmotic pressure.

Experimental

Materials and Device

Polycarbonate (PC) ($d=1.2 \text{ g/cm}^3$)



Polycarbonate

Commercial name: LEXAN OQ1026 Risen

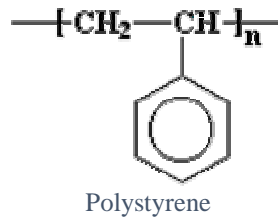
Company: SABIC® (KSA)

Melt Flow Index MFI: 11g/10min (250°C/1.2Kg)

Polystyrene (PS) ($d=1.05 \text{ g/cm}^3$)

Commercial name: SABIC® (KSA) 125PS

Company: SABIC® (KSA)



Melt Flow Index MFI = 7g/10min (200°C/5Kg)

Chloroform ($d=1.48 \text{ g/cm}^3$), sodium hypochlorite solution (NaOCl) ($d=1.25 \text{ g/cm}^3$, 14%), HCl solution (1N), NaOH solution (1N), isobutanol solution ($d=0.8 \text{ g/cm}^3$), sodium metabisulfite solution ($\text{Na}_2\text{S}_2\text{O}_5$ 1%).

UBBELOHDE viscometer, Stainless steel knife, Osmometer instrument

Thickness test instrument

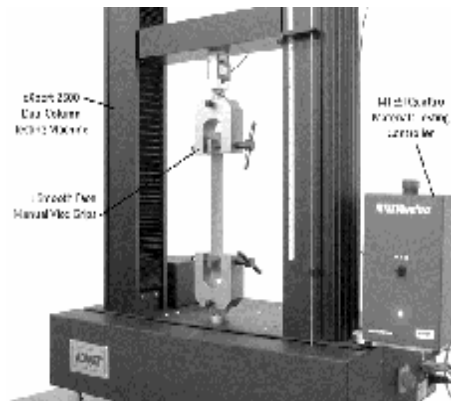
(Digimatic Caliper
Mitutoyo 500-196)



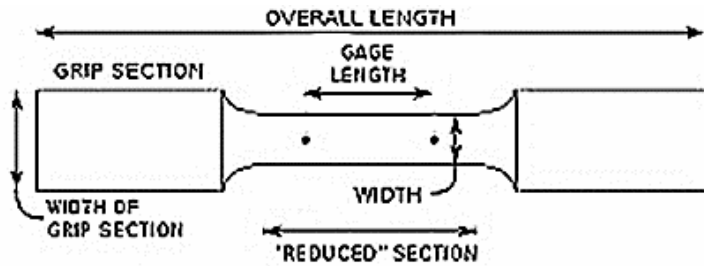
Tensile test machine

Testometric M350-10KN

The Testometric Company
Ltd Rochdale UK)



Standard tensile test specimen (ASTM E8)



Gauge length: 1.2 cm

Width: 0.8 cm

Thickness: 0.25 cm

Overall length: 8 cm

Length of grip section: 3 cm

Width of grip section: 2 cm

Length of reduced section: 3 cm

Membrane preparation

Different polymer solution was prepared by dissolving polycarbonate in chloroform to achieve homogenous solutions, then the solution warming and casting was done on glass plate by casting stainless steel knife to achieve the same thickness in all of the membrane and achieve membrane with free defects (bubble) [8,9].

The solvent was evaporated from the casting solution, then the produced membrane was separated from the glass plate and saved in sodium metabisulfite solution ($\text{Na}_2\text{S}_2\text{O}_5$ 1%) in a cool dark place [10,11].

Chemical properties of membrane

▼ Chlorine Tolerance

Membrane samples immersed for 24 h in different aqueous chlorine solution (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 to 10). The pH of the solutions controlled by addition of NaOH (1N) or HCl (1N) 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 was dried with tissue papers to remove the residual isobutanol on the membranes. The mass of the samples before and after immersing in isobutanol was measured using a digital microbalance. The porosity of the membrane P% was defined as the pore volume divided by the total volume of the membrane as follow in equation 1:

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

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

w_d : mass of dry membrane (g).

ρ_i : isobutanol density (0.802 g/cm³).

ρ_p : polyamide membranes density (g/cm³) [14].

▼ Pore size

Bubble point test was used to determine the 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 $\Delta p = p_1 - p_2$ is given by the following equation 2:

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

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].

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

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

The relative viscosity is obtained from equation 3:

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

t : flux time of polymer solution (sec).

t_0 : flux time of solvent (sec).

K_{wert} -Value is obtained from equation 4:

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

η_{rel} : relative viscosity.

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

$K_{wert}\text{-Value}=1000 \times k$

The intrinsic viscosity obtained from equation 5:

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

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

$$[\eta] = K.M_v^\alpha \quad (6)$$

Where K and α are constant [17].

Mechanical properties of membrane

▼ Tensile strength and strain

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

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

$$\sigma = \frac{F}{S} \quad (7)$$

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

S: specimen area (cm^2) = b_{specimen width (cm)} * δ _{specimen thickness (cm)}

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

$$\varepsilon = \frac{L-L_0}{L_0} = \frac{\Delta L}{L_0} \quad (8)$$

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

L : instantaneous length (cm).

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

$$E = \sigma/\varepsilon \quad (9)$$

Membrane application

To determine the polystyrene molecular weight, we used the prepared PC membranes (as semipermeable membrane) by osmometer instrument as shown in Figure 1, to know its osmotic pressure. The osmotic pressure is the pressure exerted by the column of a solution of height h that is shown in equation 10:

$$\pi = \rho \cdot g \cdot h \quad (10)$$

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

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

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

After knowing the osmotic pressure of the 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 is shown in the following equation 11:

$$\pi = c \cdot R \cdot T = c_1 \cdot R \cdot T / M_n \quad (11)$$

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)[20].

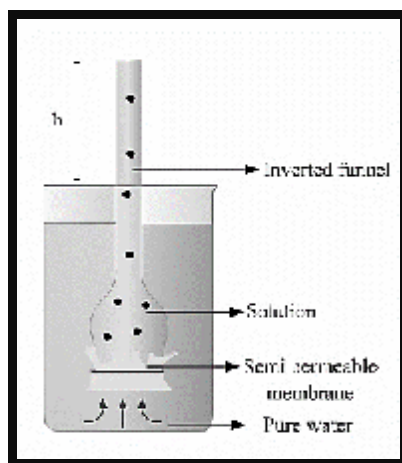


Figure 1: Osmometer instrument

Results and Discussion

Membrane preparation

Polymeric solutions of PC prepared with different concentration, then choosing the perfect membrane based on free defect (holes) and has acceptable thickness. The prepared membranes is shown in Table 1:

Table 1. Relationship between polymer solution concentration and prepared membrane.

Polymer solution concentration%(w/v)	Prepared membrane, thickness(mm)	Result
From 1% to 5%	Top-layer with defects (gaps, bubbles), weak and extremely thin	Bad for membrane formation
7% and 9%	Top-layer without any visible defects, thin (0.02-0.05 mm)	Good for membrane formation
10% and 12%	Top-layer without any visible defects, thick (0.09-0.11 mm)	Good for membrane formation
12%	Very difficult to polymer solving in the solvent	-

As followed in Table 1, the perfect polymer solutions concentration to prepare membrane are (7%, 9%, 10%, 12%) with free defect top-layer.

Chlorine tolerance and pH rang membrane

Four membranes were prepared PC (7%, 9%, 10%, 12%) and tested for chlorine tolerance and pH rang, the experimental showed that the higher chlorine tolerance and higher pH rang was for PC (10%, 12%)

membrane, that means the membrane will be damage under pH = 3, and will be damaged above pH = 10, as shown in Table 2:

Table 2. Chlorine tolerance and pH rang for prepared membrane

PC membrane	Chlorine tolerance (ppm Cl)	pH rang
PC 7%	2000	From 5 to 9
PC 9%	3000	From 5 to 9
PC 10%	4000	From 3 to 10
PC 12%	4000	From 3 to 10

Membrane porosity and pore size

Four membrane were tested for porosity, and the results showed that when membrane thickness increases, the porosity will be decreased and the pore membrane size will be smaller, that means when the polymer solution concentration increases, the solution density will be increased, that leads increase in membrane thickness and the pore size will be decreased, that is described in Table 3:

Table 3. Porosity and pore size for prepared membrane.

PC membrane	Porosity %	Pore size (μm)
PC 7%	68	1
PC 9%	63	0.8
PC 10%	55	0.4
PC 12%	43	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 knowing the time of solution and solvent flux in the instrument by using equation (3).

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

Then determination of intrinsic viscosity by using equation (5), and the determination of viscosity molecular weight by using equation (6), they are described in Figure 2.

Where: $\alpha = 0.82$

$k = 0.000226$ (100ml/g)

K_{wert} -Value = $1000 \times k$

t_0 (formic acid) = 11.87 (sec)

We obtained that $K_{\text{wert}}\text{-Value (PC)} = 18.5$

As shown in Figure 2,3,4, every relative viscosity, intrinsic viscosity and viscosity molecular weight increased by increasing of polymer solution concentration.

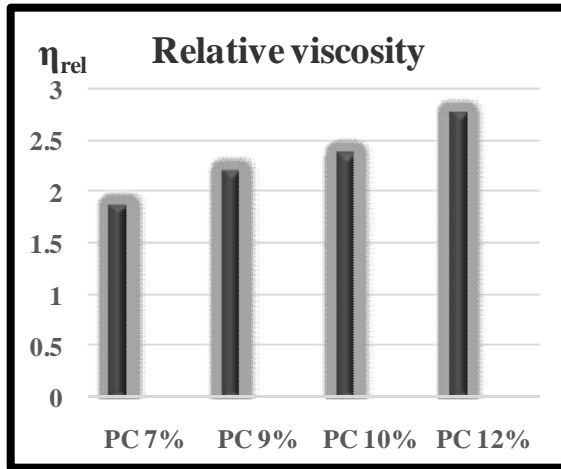


Figure 2. Relative viscosity for prepared PC solutions

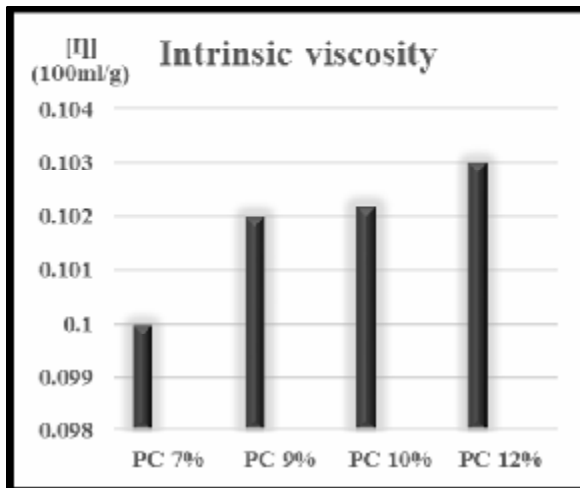


Figure 3. Intrinsic viscosity for prepared PC solutions

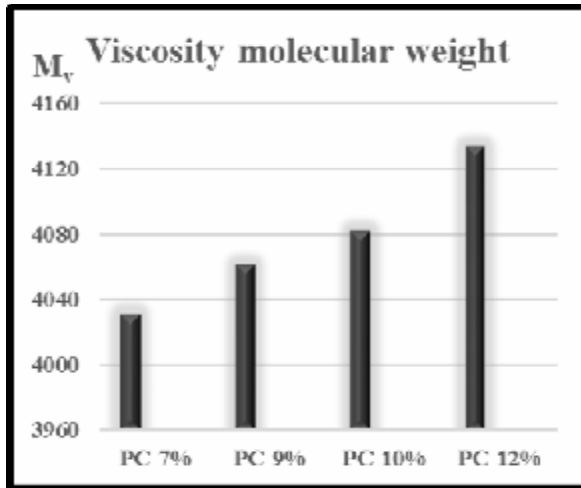


Figure 4. Viscosity molecular weight for prepared PC solutions.

Tensile strength, Strain and Young's Modulus

Tensile test machine is used for determination of tensile strength, strain and Young's Modulus, which are 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 5:

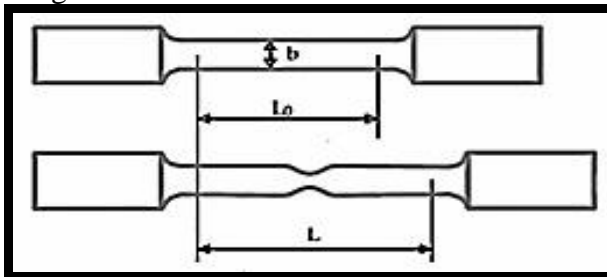


Figure 5. Standard tensile test specimen

The result shows, that PC (12%) membrane have the higher tensile strength and strain compared to other membrane, but it has the lowest Young's Modulus (stiffness), also the result showed that the strain value were very small that means the polymer is brittle, that is shown in Figures 6,7,8:

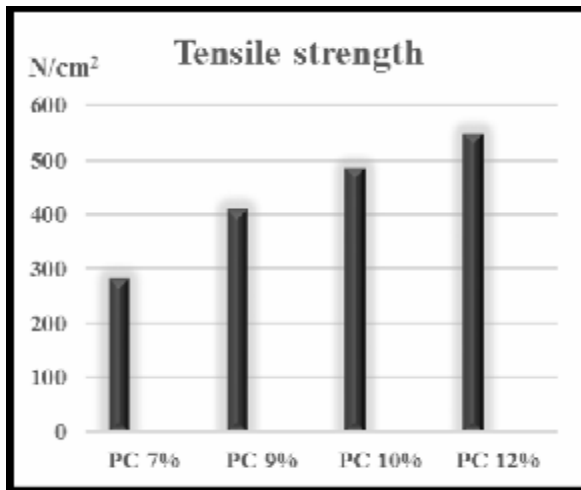


Figure 6. Tensile strength for prepared membrane

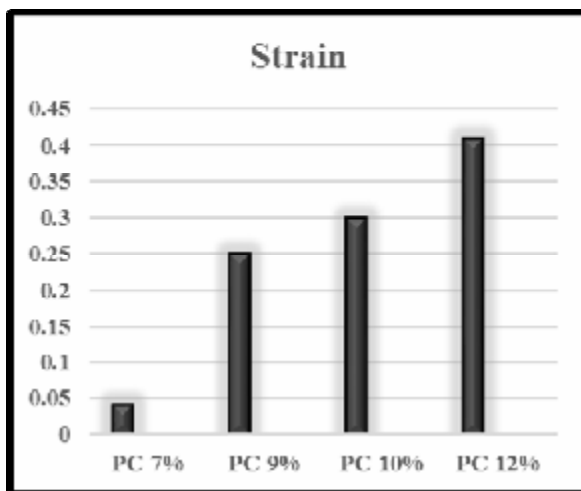


Figure 7. Strain for prepared membrane

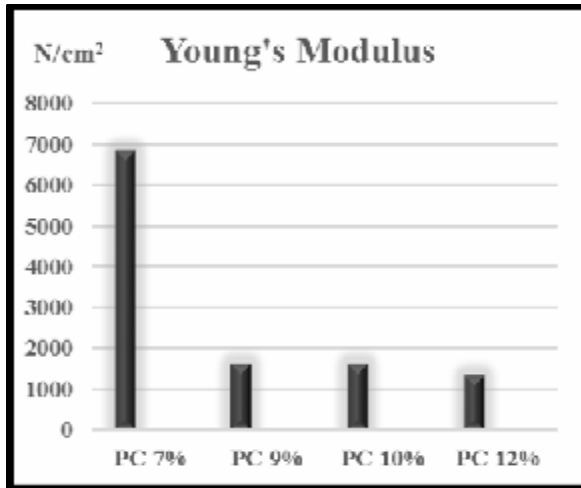


Figure 8. Young's Modulus for prepared membrane

Polystyrene molecular weight

The determination of polystyrene molecular weight, of that prepared of polystyrene solution (9g/100ml).

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

$$h=0.05 \text{ cm}$$

By using equation 10: the osmotic pressure for polystyrene solution is:

$$\pi = \rho \cdot g \cdot h \quad (10)$$

Where: density (PS 9%) = 0.93 g/cm^3 .

The osmotic pressure for polystyrene solution is $\pi = 55 \text{ (dyn/cm}^2\text{)}$.

By using equation 11:

$$\pi = c_1 \cdot R \cdot T / M_n \quad (11)$$

Where:

$$c_1 = 90 \text{ (g/1000 ml)}$$

$$R: 0.082 \text{ (atm/mol.K)}$$

$$T: 298 \text{ (K}^0\text{)}$$

The molecular weight of polystyrene is $M_n = 10101 \text{ (g/mol)}$.

Conclusions

The result show in this article:

- ✓ The suitable polymer solutions concentration for preparing membrane are (7%, 9%, 10%, 12%) with free defect top-layer.
- ✓ The higher chlorine tolerance and PH range was for PC (10%, 12%) membrane.
- ✓ When membrane thickness increases, the porosity will decrease and the pore membrane size will be smaller.
- ✓ Relative viscosity, intrinsic viscosity and viscosity molecular weight increase by increasing of polymer solution concentration.
- ✓ PC (12%) membrane have the higher tensile strength and strain compared with other membrane, but have the lowest Young's Modulus.
- ✓ Polystyrene solution (9g/100ml) and molecular weight is 10101 (g /mol).

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