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Studies for the heat effects on permeability of some semi-permeable membranes

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Abstract: The development of water purification and sea water desalination technologies is now very essential. Osmosis is the phenomenon of water flow through a semi-permeable membrane that blocks the transport of salts or other solutes through it. The enhancement of permeability of these membranes was the target of the current work. The effects of heat treatment on properties of some semi-permeable membranes during casting have been studied. A special osmosis cell has been designed and used to measure the flow rates across Cellulose Acetate (CA) and Cellulose Triacetate (CTA) membranes. 150 ^{o}C to 200 ^{o}C was the temperature range of membrane`s properties examinations. It was found that the flow rate across the CTA membranes increase at casting temperature of 200 ^{o}C, while CA membranes showed higher flow rate at 170 ^{o}C.

Key/words: Cellulose acetate; Cellulose tri-acetate; Semi-permeable membranes.

1.Introduction

Contaminated water and poor sanitation are linked to transmission of diseases. Inadequate management of urban, industrial and agricultural wastewater means the drinking water of hundreds of millions of people is dangerously contaminated or chemically polluted [1]. Natural presence of chemicals, particularly in groundwater, can also be of health significance, including arsenic and fluoride, while other chemicals, such as lead, may be elevated in drinking water as a result of leaching from water supply components in contact with drinking water [2]. Therefore, the development of water purification and sea water desalination technologies is now very essential, not only for facing water pollution, but also for facing the dangerous climate changes. These technologies, basically, built on a physical phenomenon called Osmosis. Osmosis is a fundamental effect in all biological systems [3]. It is applied to water purification and desalination, waste material treatment, and many other chemical and biochemical laboratory and industrial processes. When two water (or other solvent) volumes are separated by a semi-permeable membrane, water will flow from the volume of low solute concentration to the volume of high solute concentration.

The flow may be stopped, or even reversed by applying external pressure on the volume of higher concentration. In such a case the phenomenon is called reverse osmosis. Semi-permeable membranes are the principal axis of the osmosis process. The quality of the membrane identified the activity of the water purification mechanism. Hence, the selection of good membrane is the first step for a construction of osmotic water purification system. The known materials used for manufacturing semi-permeable membranes are too limited. Chemists did great efforts to prepare new acceptable materials for production of qualified semi-permeable membranes [4-7]. Reverse osmosis is now the most acceptable technique for both water purification and sea water desalination. Types of reverse osmosis membrane`s materials are listed down:

1 - Cellulose Acetate (CA) Membranes

It has a pore size around 100 nm, and an ionic selectivity that allows it to reject ions such as Na and Cl but allow smaller molecules such as H and COO to pass through[8].

2- Polysulfone Membranes

The pore size is around 50 nm and the ionic selectivity is similar to that of CA membranes.

3- Polyamide Membranes

They have a higher electrical resistance and lower flux. They also suffer from a high fouling rate, meaning they blocked up faster than others.

4- Polyamide-Imide (PAI) Membranes

The pore size is around 50 nm, and the ionic selectivity is similar to that of CA membranes.

5- Polyethersulfone (PES) Membranes

They have pore size around 50 nm[9].

6- Polyimide Membranes

They have a very low flux, and are prone to fouling by particles [10].

7- Polysulfone (PSF) Membranes

The pore size is around 50–80 nm [11].

8- Polyvinylidene Fluoride (PVDF) Membranes

They have a very low resistance to fouling by particles but are very resistant to acidic solutions used as agent in affinity chromatography [12].

9- Polyethyleneimine (PEI) Membranes

The pore size is around 50–80 nm [12].

From the above list, it is clear that cellulose acetate still the better selection as material for casting semi-permeable membranes. But it has low permeability which restricts its wide usage. Other polymers have serious disadvantage too. Therefore, the aim of the current work is to enhance the permeability of some traditional semi-permeable membranes by applying some physical treatments during manufacturing.

2. Materials and methods

2.1. Materials

Cellulose acetate (CA), Cellulose triacetate (CTA) was purchased from Sinopharm Chemical Reagent Co., Ltd.; (Shanghai, China). Acetone, Chloroform and Glacial acetic acid were obtained from the local company Al-jumhuria.

2.2. Fabrication of Membrane

All used membranes in this work were fabricated by casting technique. The casting solution was prepared by blending 0.2 g of semi-permeable polymer with 20 ml of solvent and 0.02 ml from Glacial acetic acid is added under constant stirring speed for 6 hrs at room temperature. Then, the casting solution was poured into a Petri dish of 12 x12 cm and was left exposed to air stream in a gas chamber until full evaporation of the solvent, hence the membrane was self-separated from the dish.

The thickness of such membrane was found around 40 µm. These steps are shown in Fig.1. The opinion behind thermal effect on membrane during fabrication raised due to the strong changes in the chain structure of a polymer due to thermal effects on the polymers during fabrication [13, 14].

Figure 1. The casting steps for semi-permeable membranes.

2.3. Heat processing of membranes

The permeability of a membrane may be changed by controlling the evaporation rate of the solvent. The evaporation rate can be adjusted by left the casted solution to evaporate under different temperatures in a gas chamber. Table 1 indicates the symbolic names of the processed membranes at different temperatures.

Table 1 The symbolic names of the membrane samples which are processed at different temperature.

CA0	Casted at room temp.	**CTA0**	Casted at room temp.
CA2	Casted at 150^0c	**CTA2**	Casted at 150^0c
CA3	Casted at 170^0c	**CTA3**	Casted at 170^0c
CA4	Casted at 200^0c	**CTA4**	Casted at 200^0c

2.4. The experimental measurements

2.4.1. Permeability measuring system

In the field of water filtration by means of a semi- permeable membrane, the permeability of the membrane is the most important physical parameter. This parameter describes the efficiency of the membrane. The flow rate gives a numeric value for the efficiency too. Therefore, the permeability measuring system should measures the volume of water flow during definite time interval. A simple measuring system was designed and fabricated to measure the flow rate of water through a

semi-permeable membrane. Fig. 2 is a schematic diagram for the used measuring osmosis cell.

2.4.1.1. Operation of the osmosis cell

The osmosis cell as shown in Fig.2 is used to

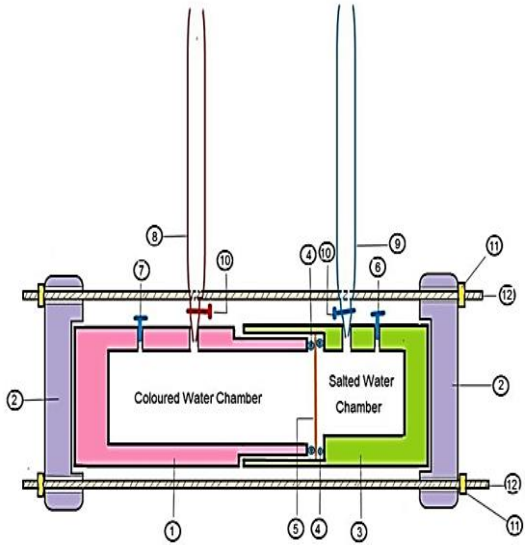

Figure 2. The used osmosis cell to measure the flow properties through a membrane

measure the flow rate of water through a membrane, and then it is easy to find the flow rate per unit surface area of the membrane at

known concentration of the salted water. After inserting the membrane and the sealing rubber rings, the two chambers should fit to each other and to the pressing bases 2, and then the long screws 12 and nuts 11 should be tighten hardly to prevent leakage. The colored water (feed solution) chamber and the salted water (draw solution) chamber are initially filled by placing small funnel at top of burettes. In order to recognize the performance of the cell and the membrane, the non-salted water was colored by a water base dye, while the salted water is kept uncolored.

2.4.2. Differential Scanning Calorimeter

Differential Scanning Calorimetry (DSC) is an analytical technique which measures the heat flow into or out of a sample as a function of time and/or temperature. Plots showing differences in heat flow between a sample and reference, as a function of time or temperature, yield in- formation on thermal transitions in a sample due to melting, crystallization, chemical reactions, glass transitions, and other exo-thermic (heat evolving) and endothermic (heat absorbing) transitions[15]. DSC measurements of membrane`s materials were performed using a Shimadzu DSC-60 (Japan). A single ascending scan from 20 to 150°C/min at an annealing temperature of 5°C/min was used for the measurements. The Tasks software that came with the instrument was used to analyze the data.

2.4.3. Infrared spectral analysis

To investigate the function groups of the samples, FTIR spectral analysis were followed

using FTIR spectrophotometer (Mattson 5000, USA) for all the prepared samples in the wave-number range 400-4000 cm^{-1} at 2.0 cm^{-1} resolution. Acetyl, ester, carbonyl, and hydroxyl groups were studied. To obtain high-quality spectra, clear transparent films were obtained and measured just after preparation

2.4.4. Mechanical property

The mechanical properties of the membranes were measured by fixing their ends between the two jaws of the highly customizable mecha-nical stretching system, which is designed, assembled and calibrated locally. Tensile testing was used to examine the effect of different temperatures during the heat processing on mechanical properties of the prepared membrane. The sample is subjected to a known tensile force. An elongation occurs in the membrane. By increasing the applied force, the length of the membrane increases too until it breaks. The applied stress and the produced strain are recorded automatically by specially written software. The tensile modulus (Y) was calculated as the stress (σ) divided by the strain (ε). The used measuring system is locally made and calibrated using soft and stiff springs.

2.4.5. X ray Diffraction Spectroscopy (XRD)

X-ray diffraction measurements of all samples were done by a Shimadzu X-ray diffractomete (the apparatus type Dx-30, located at Metallurgy institute, El Tebbin, Cairo, Egypt). The synthesized samples were crushed to fine peels in an agate mortar and analyzed with an X-ray diffractometer. X- Ray diffractometer operates at 40 kV as the accelerating voltage and 30 mA current in 0.02 second intervals over a 2-theta range of 50 to 750 with a time of 0.4 s.

Table 2 Some mechanical constants of the heat processed cellulose acetate membranes.

	Lo (m)	ΔL (m)	ε	F (N)	A (m^2)	σ (N/m^2)	Y (N/m^2)
CA0	0.054	0.009	0.167	0.0686	0.00124	55.3	331.6
CA2	0.05	0.004	0.08	0.0686	0.00075	91.5	1143.3
CA3	0.0525	0.0015	0.029	0.0686	0.000945	72.6	2503.2
CA4	0.034	0.003	0.088	0.0686	0.000408	168	1910.6

3. Results and Discussion

3.1. Effect of casting temperature

The casting temperature may cause changes in the physical properties of the semi-permeable membranes, as determined by DSC. **Fig.3a** depicts the DSC measurements of as spun and thermally processed samples under various conditions for CA (CA0, CA2, CA3 and CA4). Cellulose acetate is relatively resistant to flame and also has a high melting point so that it melts and is carbonized at 230 to 300℃[16]. It is clear that the samples which processed at higher temperatures lost its solvent soon and has solidified early and during the rest of processing time the sample started its decomposition. Note that, only crystalline polymers show clear melting peak as the non-processed sample CA0.

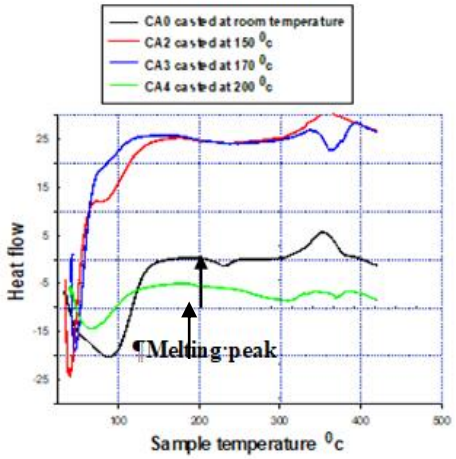

Figure 3a. DSC analysis of thermally processed CA membranes.

Other processed samples lost their crystals due to the processing near the melting point at about 230 °C. **Fig.3b** shows this conclusion, where all samples show long ordered range, but absence of crystals. **Table 2** supports the expected decomposition of CA membrane when the processing temperature became close to the melting temperature for longer time while it was in its solid phase. The possible decomposition reduced the tensile modulus of the sample CA4. Starting decomposition means weakness of molecular bonds and hence molecules can now vibrate with broaden range of frequencies close to the original characteristic frequency.

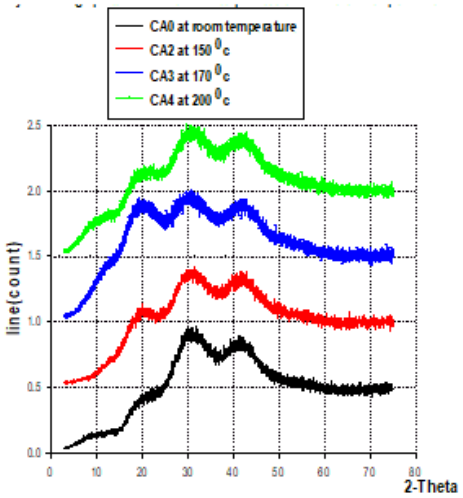

Figure 3b. X-ray diffractograms of CA membranes processed at different temperatures.

Fig.4 presents the IR spectrograph of the processed CA membranes at different temperatures. The sample CA4 which casted at 200°C shows peaks broadening, specially around 1100 cm^{-1}, this in turn supports the suggestion of starting a chemical decomposition if CA membranes are casted at temperatures close to the melting temperature.

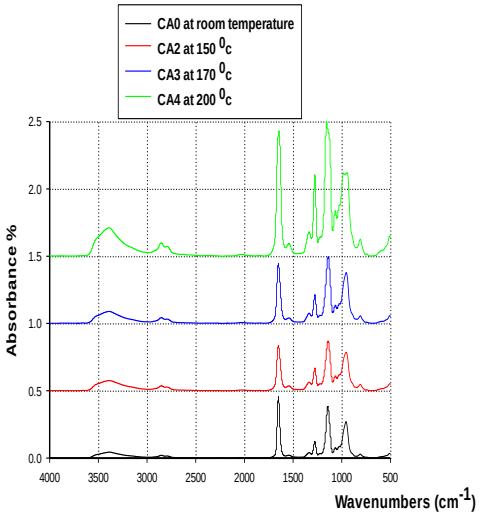

Figure 4. IR absorption spectrum of thermally processed CA at different temperatures.

The above discussion demonstrates the response of CA membranes to the applied temperature during their processing. But, did these responses support the aim of this work? The answer is related to the flow rate through the membrane. Recalling Fig.2, which shows the structure of a forward osmosis (FO) cell that can be used to measure the volume of water, flowed through the membrane from the feed solution to the draw solution within certain time interval. By this information one can compute the flow rate through a membrane. The volume of water flowed through a membrane does not depend on the type of used semi-permeable material, but also on the surface area, thickness, temperature of surrounding media of the membrane and the salt concentration of the draw solution. That last factor is very effective parameter on the flow volume and flow rate. Therefore, the osmosis cell in Fig.2 was used to measure the flow volume by draw solutions with different salt (NaCl) concentration. Fig.5 presents the flow volume as function of time across a CA0 membrane at different salt concentration of draw solution. Fig.5 shows that draw solution of 10% salt concentration gives reasonable flow volume which can be measured with better accuracy. Salt concentrations higher than 10% showed values too close to those given by the concentration 10%.

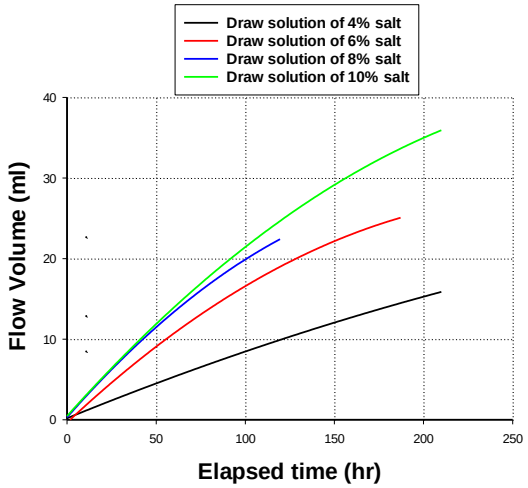

Figure 5. Flow volume through CA0 membrane as function of time.

Hence draw solution (DS) of 10% salt concentration was used in all osmosis measurements by the cell shown in Fig. 2 through the current work. Now it is the time to examine the effect of processing temperature on the flow volume. Fig. 6 presents the FO flow volume across the samples CA0, CA2, CA3 and CA4. The observed trend in Fig.6 is the increasing of flow rate by increasing the processing temperature. The sample CA4 which processed at 200 ^{o}C shows irregular shift from the common trend. This shift may be due to the case of starting decomposition of this sample. Also, it is clear that casting CA at 170 ^{o}C will produce membrane of better permeability. The effect of casting temperature on the physical properties of the cellulose triacetate (CTA) membranes has been studied too.

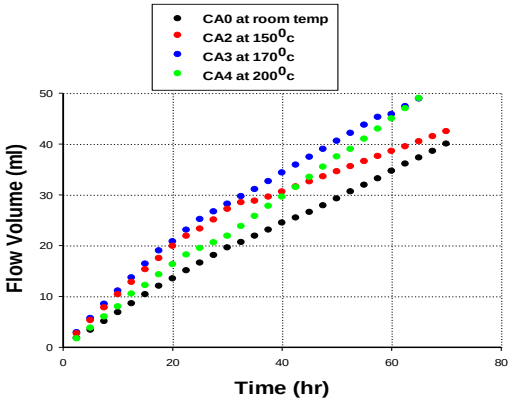

Figure 6. Representation for the effect of processing temperature on the FO flow across CA membranes.

Fig. 7 shows the DSC graph of CTA membranes that are casted at different temperatures as like those used for CA membranes. The DSC analysis of CTA membranes cleared that the casting temperature does not affect the melting point at 297^{o}C, while decomposition of CTA starts at 177^{o}C[17].

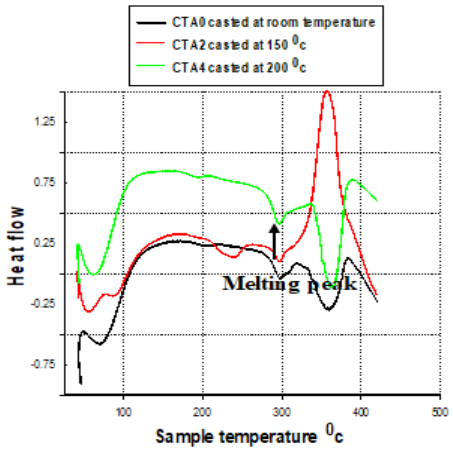

Figure 7. DSC graph of CTA membranes were casted at different temperatures.

So, it is expected to see the same physical behaviors as that of CA. For example, the CTA

membrane that casted at 170^{o}C has the better tensile strength. The sample CTA 4 that is casted at 200^{o}C shows less strength for the same reason which suggested for the case of CA4, i.e, CTA4 started decomposition before other samples where it was at 200^{o}C much close to the melting point. Table 3 indicates this explanation. Although sample CTA4 was started its decomposition, it showed perfect IR spectral coincidence with other CTA samples as shown in Fig.8. This difference than CA4 at the same conditions may be due to the difference in the crystalline state of the two samples. Fig.10 shows the broadening of the amorphous hump of CTA4 than those of CTA2 and CTA3 and even CA4. The effect of processing temperature on the forward osmosis (FO) of CTA membranes is shown in Fig.9. The started decomposition membranes CTA4 and CTA3 show better FO flow. This may be due to opening of more pores which were blocked before decomposition.

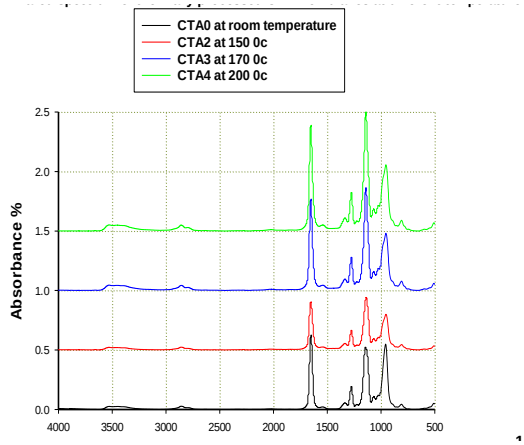

Figure 8. IR spectra of CTA membranes which were thermally casted.

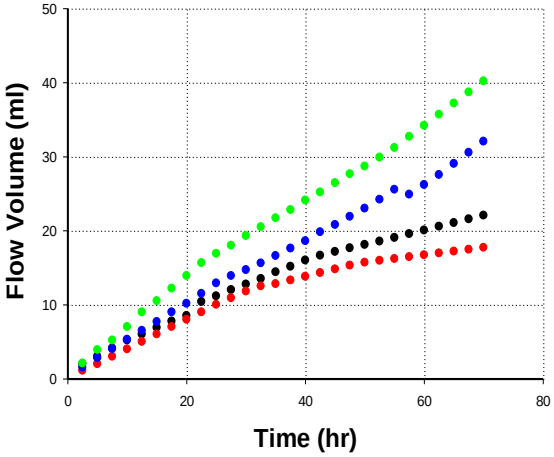

Figure 9. FO flow of CTA membranes that are casted at different temperature.

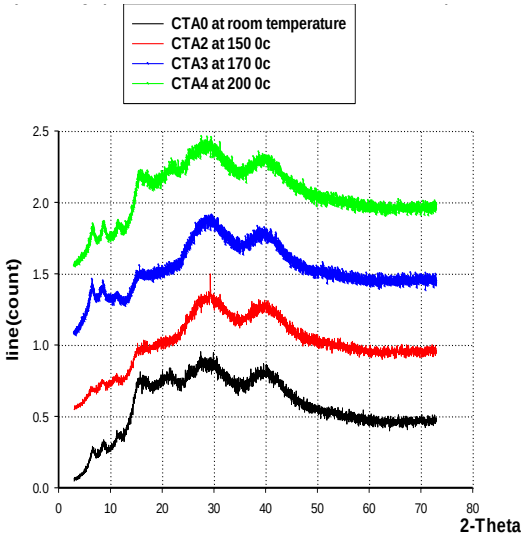

Figure 10. X-ray diffraction by CTA membranes casted at different temperature.

Table 3 Some mechanical parameters for the thermally processed cellulose triacetate membranes.

	L_0 (m)	ΔL (m)	$\mathscr{E}$	F (N)	A (m^2)	σ (N/m^2)	Y (N/m^2)
CTA0	0.057	0.006	0.105	0.0686	0.00114	60.18	571.67
CTA2	0.055	0.004	0.073	0.0686	0.00099	69.3	949.3
CTA3	0.046	0.003	0.065	0.0686	0.0005	137.2	2110.8
CTA4	0.046	0.004	0.087	0.0686	0.0006	114.3	1314.2

Samples used in these figures were examined by scanning electron microscope (SEM) as a trial to proof the validity of the above deduction, but because of the high smoothing of samples surfaces, no distinct details were observed.

4. Conclusions

The enhancement of permeability of these membranes was the target of the current work. A special osmosis cell has been designed and used to measure the flow rates across different types of semi-permeable polymer membranes. Samples from these membranes were exposed to thermal effects during processing casting. 150 ^{o}C to 200 ^{o}C was the temperature range of membrane`s properties examinations. It was found that the flow rate across the CTA membranes increase at casting temperature of 200^{o}C while CA membranes showed higher

flow rate at 170 ^{o}C. Little variations were detected for the crystalline state, melting points and mechanical strength of thermally casted CA and CTA membranes.

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