Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2017, 4(9):520-527**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Microwave Post-Treatment of PES Hollow Fiber Membranes immersed in NaCl Solution

K.A. Abed[1]*, Nahed A. El Mahallawy[2], Mohammed H. Sorour[3], Mahmoud A. El-Bayoumi[1], Yomna O. Mostafa[1]

[1]Mechanical Engineering Dept., Engineering Research Division, National Research Centre, Dokki, Cairo, Egypt
[2]Design and Production Engineering Dept., Faculty of Engineering, Ain Shams University, 1 El Sarayat St., Abaseya, Cairo, Egypt
[3]Chemical Engineering and Pilot Plant Dept., Engineering Research Division, National Research Centre, Dokki, Cairo, Egypt

Abstract Polyethersulfone (PES) hollow fiber membranes (HFMs) are widely used in diverse fields such as biomedical and numerous water treatment applications as ultrafiltration (UF) and nanofiltraton (NF). Tuning of surface morphology and mechanical characteristics is essential for successful performance, which is related to the target application. In this paper, microwave (MW) irradiation has been utilized as a post-treatment technique for the tuning of the above mentioned characteristics. Investigations are centered on variation of the saline bath containing different concentrations of sodium chloride (NaCl) (1-4 wt%) as an external heat transfer medium at a specific temperature and duration. The MW irradiated HFMs have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and numerous mechanical testing parameters. Investigations in the above mentioned range indicates that at 2% sodium chloride solution concentration unique properties prevailed, where it showed a decrease of 16.13% in wall thickness and a minimum surface roughness value with 19.22% decrease when compared to the untreated HF membranes. Also, it showed highest break stress increase of about 8.8% and highest break strain increase of about 17% as well as highest tensile modulus increase of about 25.9%. In general MW post-treatment confirmed the possibility of tuning surface morphology and mechanical properties using a specified saline concentration providing the intended degree of modification to cope with the targeted application.

Keywords Stress-Strength model, modified exponential distribution, maximum likelihood estimator, minimum variance unbruised estimator, Bayes estimator

1. Introduction

Recently, membrane separation technology has attracted huge attention due to its outstanding performance, economically and environmentally. It tackles a wide spectrum of crucial applications, water desalination, wastewater treatment, dairy, pharmaceutical and textile industries, pervaporation and gas separation.

Hollow fiber membranes (HFMs)are the most efficient configuration due to its large active area to volume ratio, its mechanically self-supporting structure and its ease of processing, handling and employment [1]. HF Msmorphological structure is the main factor affecting membrane performance, therefore optimizing membrane structure, through tuning the processing material and/or their processing parameters, is a vital step to reaching the required performance. Processing parameters are needed to develop HFMs to meet the desired characteristics and performance [2], while post-treatment is introduced to remove excess solvent as well as

tailoring pore size and releasing induced stresses during production. Also, it is a method to modify and repair defects on the membrane surface resulting from processing without changing the bulk membrane structure [3].
With consideration of the limitations of drying techniques as a post-treatment using conventional heating such as air oven drying, there is a necessity for exploring the effects of microwave (MW) heating as a clean, rapid, efficient and reliable technique for post-treatment. Very limited reported endeavors are available on MW heating on membranes in general and HFMs in particular [4-8]. Mansourpanah *et al*. [9] , concluded that pure water permeability (PWP) for PES flat sheet membranes increased by increasing MW radiation (180-900 Watt).Atomic force microscopy (AFM) results showed that the membranes surface roughness (Ra) was altered after MW irradiation. It was observed that roughness decreased at small MW irradiation periods (10 seconds), but at higher exposure periods, roughness increased and a dense thick layer was formed. Also contact angle tests revealed an increment in hydrophilicity with increasing radiation duration.
Sze Yean [10], studied the effect of MW post-treatment on PES HF UF membranes morphology and performance in comparison to hypochlorite post-treatment. MW post-treated HFMs showed superior properties when compared to that of hypochlorite treated membrane which was apparent in the formation of smaller macrovoids, finger-like structure, as well as a larger boundary layer between the double finger-like structures. Ahmed *et al*. [11] and Idris *et al*. [12], compared the results of annealing and MW post-treatment in which the latter enhanced HFMs performance, hydrophilicity, reduced pore size and consequently decreased MWCO. Further research is required to cover the many gaps in this topic from different aspects, like comparing the MW post-treated and untreated membranes performance, investigating the effect of post-treatment media type and concentration and studying the mechanical properties of the treated fibers.
This paper aims at filling the gaps in the previous researches through investigating the effect of MW post-treatment in different concentrations of saline media on the mechanical and morphological characteristics of PES HFMs.

Materials and Methods

Materials

HFMs were readily prepared as a part of the “Hollow Fiber” project in the National Research Centre. A dope comprising PES polymer, poly vinyl pyrrolidone (PVP) as additive and N-methyl-2-pyrrolidone (NMP) as solvent, has been used to prepare HF membranes by dry-wet spinning technique. Prepared fibers were soaked and rinsed during and after processing by pure reverse osmosis (RO) water to remove excess solvent and additives in the membrane structure. Sodium chloride (NaCl) supplied from Chemika was used for the preparation of the post-treatment soaking solutions.

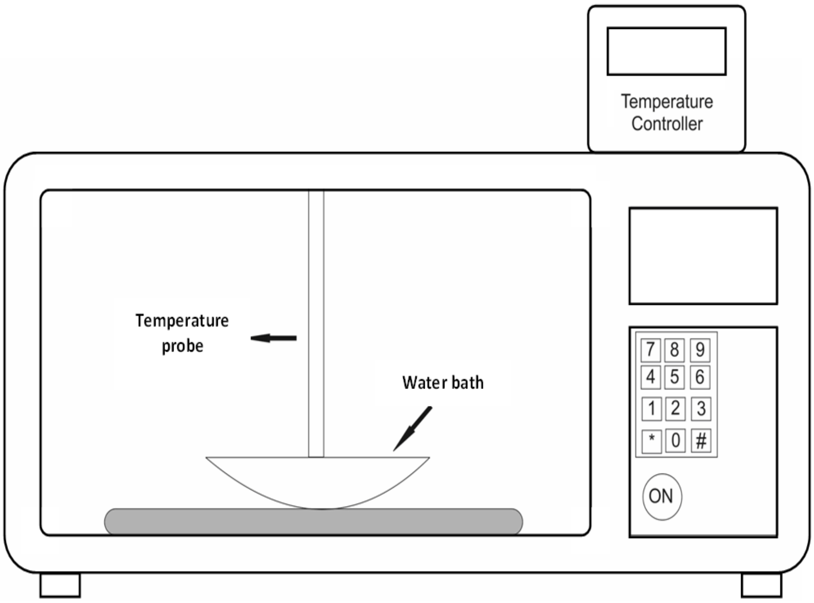


Figure 1: Schematic diagram of MW oven system equipped with the temperature controller

Equipment

A modified 2.45 GHz frequency with a rated 900 Watts of power MW oven, (DAEWOO Electron KOR-1A 6A, Korea), shown in Figure 1, has been utilized for the post-treatment of the produced HF membranes. An on-off temperature controller is attached to the MW with a temperature probe in order to control treatment temperatures.

MW post-treatment

A bundle of 30 HF membranes were cut to 30 cm long fibers and washed extensively with RO water prior to any post-treatment procedure. Meanwhile, different concentrations of NaCl solutions (1-4%) were prepared by adding an appropriate amount in RO water and ensuring complete dissolution of the salt. Subsequently, the well-washed HF membranes bundle is soaked in the pre-prepared NaCl solution, in a stress free orientation, in a 1 liter plate to be post-treated in the MW oven at 55˚C for 10 minutes.

Table 1) shows the treatment conditions represented in sample codes consisting of three parts, where the first part represents the treatment temperature while, the second part is the treatment duration and the last part is the NaCl solution concentration.

Table 1: MW post-treatment conditions

Sample code	Temperature (˚C)	Duration(minutes)	NaCl (wt%)
S0	55	10	0
S1			1
S2			2
S3			3
S4			4

Characterization of PES HF membranes

Untreated MW post-treated HF membranes are left to dry in open air for 24 hours before conducting any morphological or mechanical testing.

Scanning electron microscopy (SEM)

Morphological structures were studied by SEM imaging using JOEL JCM-6000 apparatus. HF samples were cut with the means of a sharp razor and then, fixed on the sample stage using carbon double-face tape. Morphological structure, inside and outside diameters of HF membranes as well as wall thickness were evaluated from the cross-section images.

Atomic force microscopy (AFM)

PES HF surface morphology and roughness was analyzed using 1.5 micron resolution TT-AFM workshop, equipped with a video optical microscope with up to 400X zoom. A one cm long fiber sample was fixed using a double face tape on the magnetic plate of the AFM apparatus. Vibrating scan mode was used for testing a scan area of 10µm×10µm. Roughness parameters were calculated using "Gwidyyon" software. Five samples were examined for each condition to ensure reproducibility of results.

Mechanical properties

Mechanical properties of PES HF membranes were studied using a bench top tensile testing machine, (Tinius Olsen H5kS), equipped with a 5N load cell. Testing was undertaken at 50 mm/min speed and gauge length of 100 mm. Tensile stress, elongation at break and fiber's Young's modulus were measured. The average of 5 samples readings was taken for each condition.

Results and Discussion

Morphology of PES HF membranes

SEM images of a representative untreated HFM sample (a, b) and the MW post-treated samples (c,d) in 1% NaCl solution concentration are shown in Figure 2 where a and c correspond to SEM cross sectional images while, b and d, represent HFM wall thickness images at higher magnification. The cross-sectional morphological structure demonstrates an elongated finger-like structure with a decreased sponge like layer.

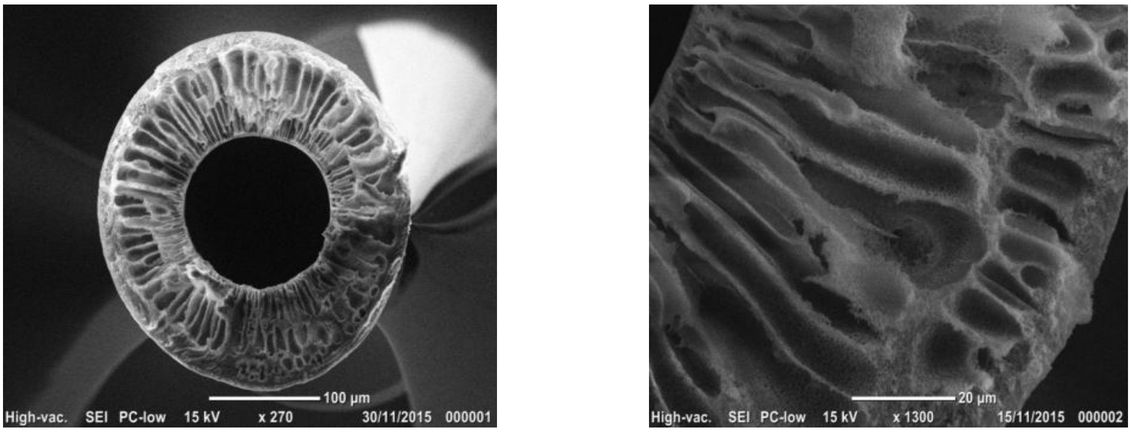
Table 2: Dimensional changes of MW post-treated PES HFMs in different sodium chloride concentrations

Sample	ΔD_o(%)	ΔD_i(%)	Δw.th (%)
S1	13.57	72.80	-34.2
S2	-7.14	4	-16.13
S3	11.79	30.40	-3.23
S4	-4.64	-0.80	-7.74

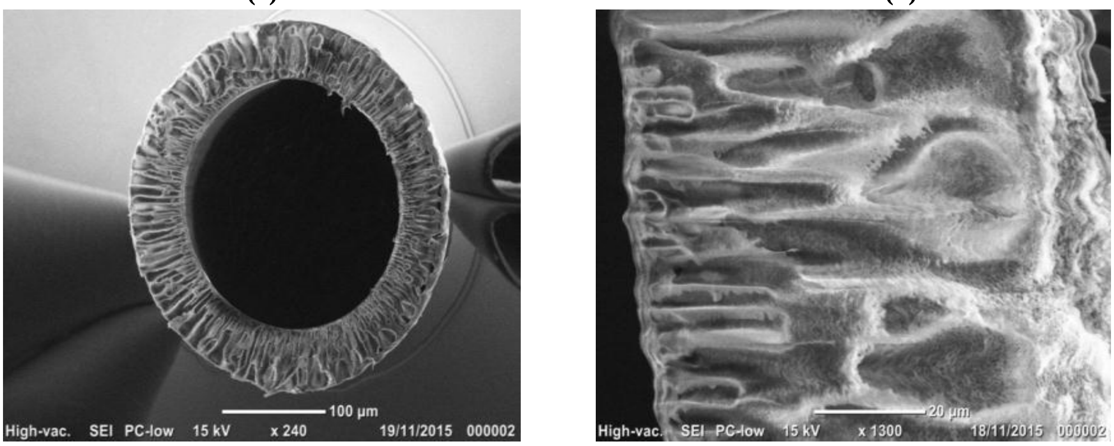
Table 2 and Figure 3, represent the changes in outer diameter (ΔD_o), inner diameter ($\Delta D_{i)}$ and wall thickness (Δw.th) of the MW post-treated samples as compared to the untreated sample. It is observed that all wall thicknesses decreased due to MW post-treatment in saline solutions at any tested concentration, with the maximum decrease of 34.2% taking place at 1% NaCl saline solution. It is noted that, morphological structure was maintained with only slight differences in fiber dimensions after treatment in saline solutions.

In general, all samples showed a decrease in wall thickness when post-treated at 55 ºC and 10 minutes duration in all tested sodium chloride concentrations where the range of change is from -3.2% to -34.2%. It should be emphasized that the highest change is observed at 1%NaCl solution concentration while the lowest is observed at 3% NaCl solution concentration.

The work of Rozzi *et al*. [13] and Anwar *et al*. [14] on the effect of MW on dilute salt solutions tends to partly support our finding. Hence, they concluded that increasing salt concentration reduces thermal heat effect of MW due to the restriction of the mobility of water molecules. In fact, MW effect using saline solution as heating media is supported by two mechanisms. The first is rotational movement of water dipoles and the second is the conducting mechanism of ionic species (ionic conduction mechanism). It seems that ionic conduction mechanism is inhibited at larger salt concentrations.



(a) **(b)**



(c) **(d)**

Figure 2: SEM images of PES HF membrane of untreated sample (a, b) and MW post-treated sample (c,d) at 55 ºC for 10 minutes in 1% NaCl solution

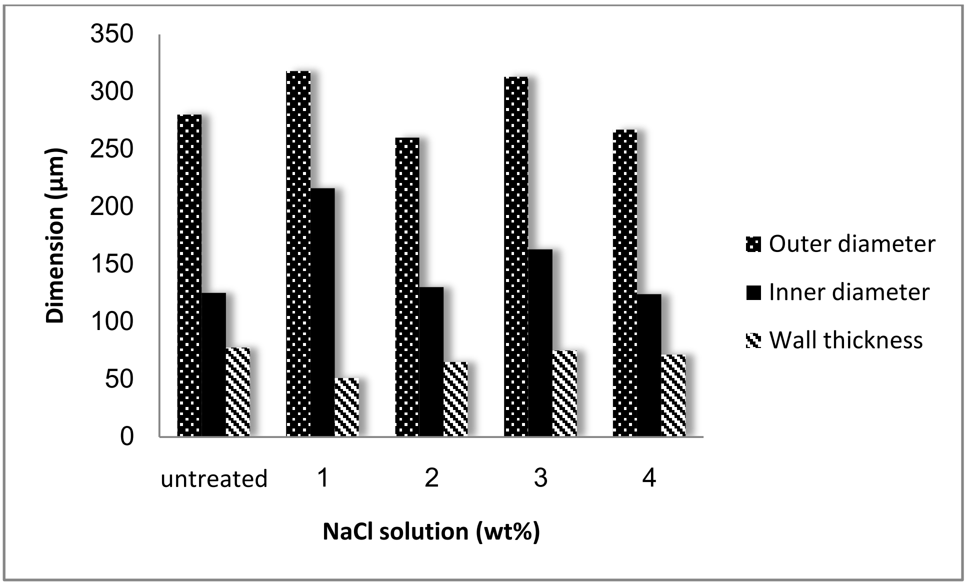


Figure 3: Dimensions of PES HF membrane of untreated and MW post-treated samples in different concentrations (1-4%) of saline solution

Surface roughness

Figure 4 shows the effect of MW post-treatment on HFMs surface roughness (Ra) in all tested NaCl concentrations at 55˚C and 10 minutes. It is observed that surface roughness increased for all NaCl concentrations with an exception at 2% NaCl solution which represents 19.2% decrease in Ra value. On the other hand, 3% NaCl solution achieved the highest roughness value of 41 nm when compared to 31.9 nm corresponding to the untreated HFM surface roughness. AFM roughness measurements show an increasing trend in surface roughness (Ra) in saline solution, which simply explains the interaction of ionic conductance and water rotational mechanism. It is important to emphasize that at 2% salt concentration there is a decrease in roughness.

Figure 5 depicts AFM 3D images of the scanned surfaces representing a moderately smooth surface of the untreated sample (a), the smoothest surface with lowest Ra at 2% NaCl solution (b) and the highest roughness achieved at 3% NaCl solution (c) due to the characteristic increased peaks and valleys.

From the application point of view, increasing surface roughness favors subsequent coating using interfacial polymerization while decreased roughness is favored for biomedical membranes and also MF and UF membranes. In the latter's case, increased roughness favors fouling tendency.

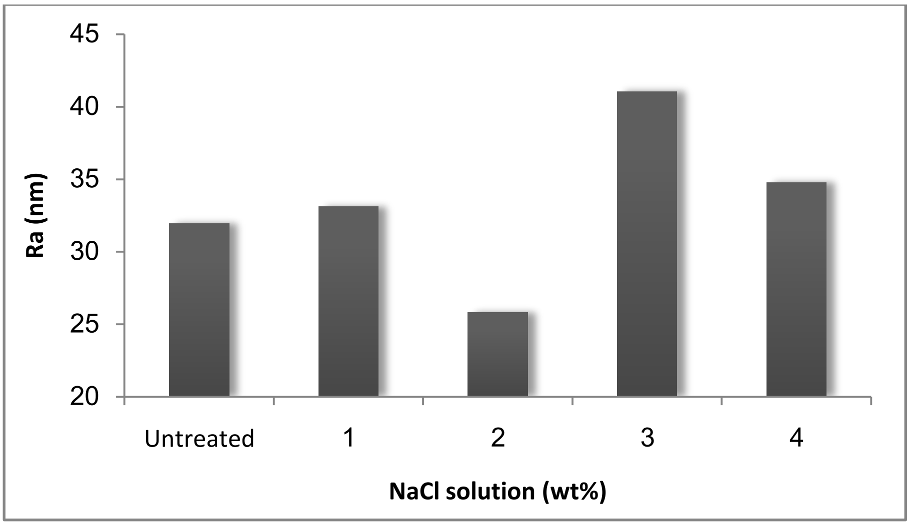
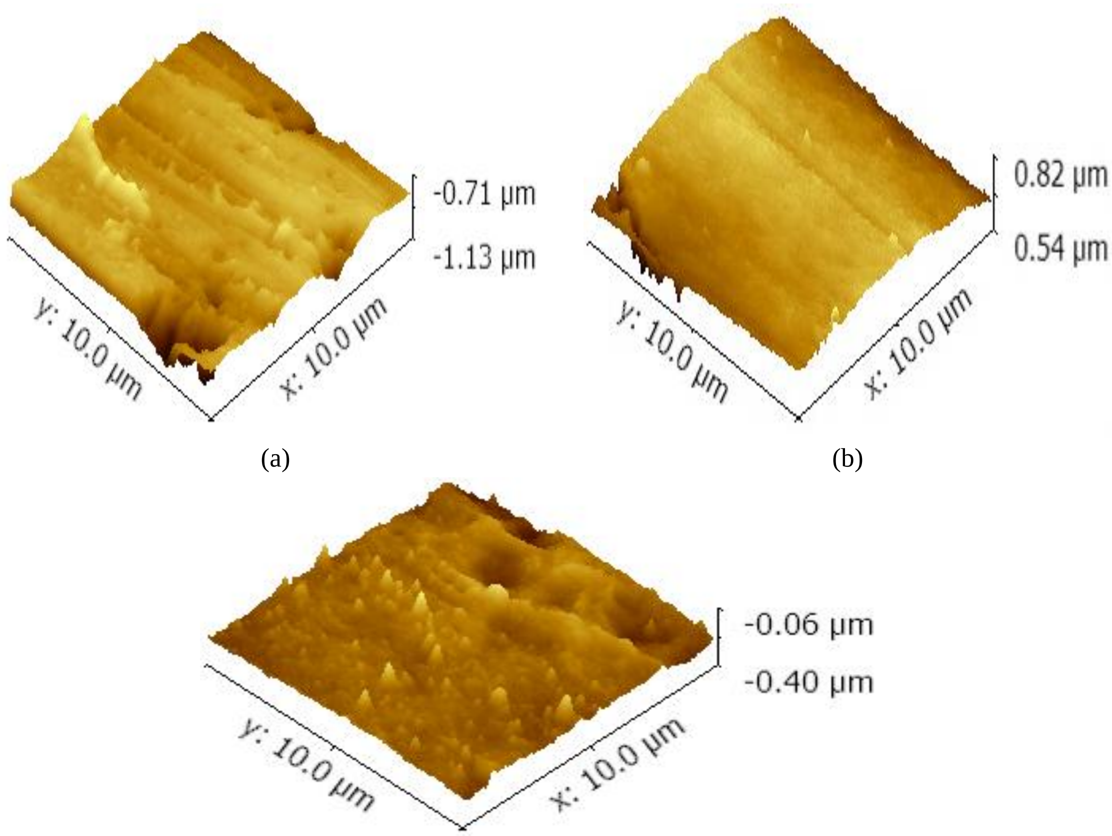


Figure 4: Surface roughness of MW post-treatment of PES HF membranes in different NaCl saline concentrations



(a) (b)

(c)

Figure 5: AFM 3D images of untreated sample (a), MW post-treated HFMs in NaCl solutions of (b) 2% and (c) 3%

Mechanical Properties

Break stress and break strain

Break stress and break strain values are represented in Figure 6. Break stress values decreased upon post-treatment with an exception at 2% NaCl solution where it increased about 8.8%. On the other hand, the maximum decrease in break stress values was achieved at 3% NaCl solution concentration. Break strain also decreased for all treated samples with an exception at 2% NaCl solution which showed maximum increase of 17%, while maximum decrease was at 1% NaCl solution.

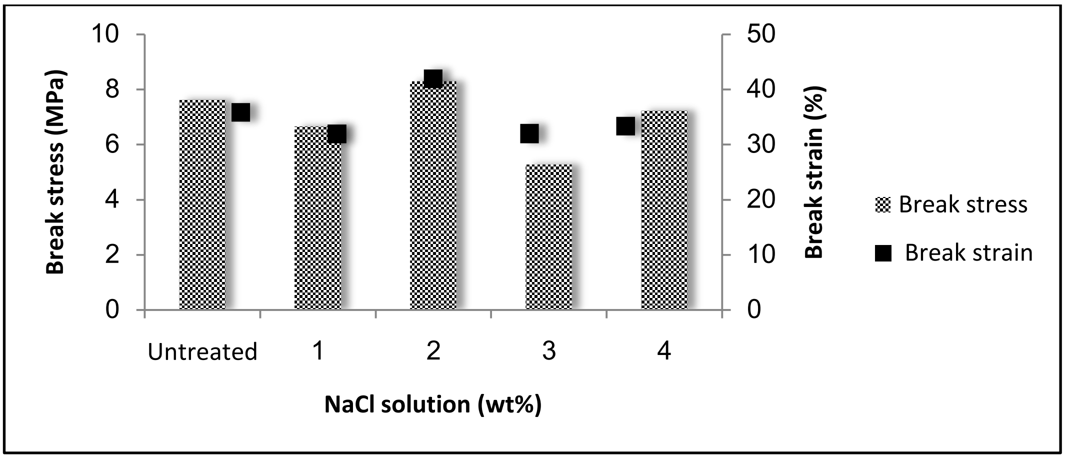


Figure 6: Break stress and break strain values of untreated and MW post-treated PES HF membranes

Modulus of elasticity

Figure 7 illustrates Young's modulus values for untreated and MW post-treated samples. Young's modulus values increased at 2% and 4% NaCl concentrations with the maximum increase of 25.9% at 2% saline solution. While Young's modulus decreased at 1% and 3% with maximum decrease of 23.8% at 3% saline solution.

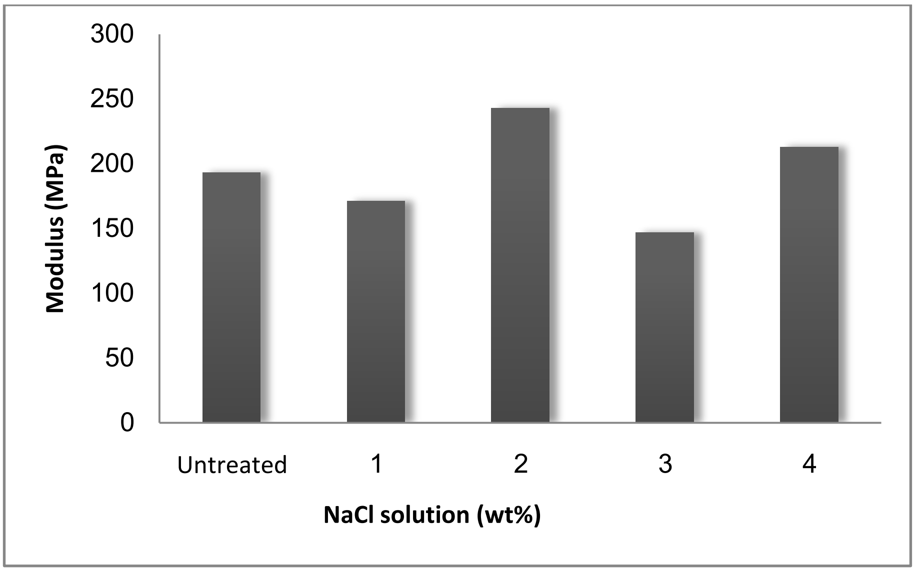


Figure 7: Young's modulus values of untreated and MW post-treated PES HF membranes

It is concluded that MW heating in saline environment show the highest Young's modulus approaching 243 MPa at 2% saline concentration, which is about 26% change. It is observed that the increased modulus is shown for 2% and 4% saline concentrations while the decrease in Young's modulus is at 1% and 3% saline concentration which basically illustrates the possible tuning of Young's modulus through selection of the appropriate medium salinity. The observed results present the contribution of the ionic conduction mechanism in the case of saline medium.

The changes in mechanical properties of MW post-treated HFMs at each NaCl concentration when compared to the untreated sample are shown in

Table 3 where $\Delta\sigma_b$, $\Delta\epsilon_b$ and ΔE denote the change in break stress, break strain and young's modulus, respectively.

Table 3: Mechanical properties changes of MW post-treated PES HFMs in NaCl solutions

Sample	$\Delta\sigma_b$(%)	$\Delta\epsilon_b$(%)	ΔE (%)
S1	-12.7	-10.9	-11.4
S2	8.8	17.0	25.9
S3	-30.8	-10.6	-23.8
S4	-5.2	-7.0	10.4

Conclusion

The effect of microwave post-treatment of PES hollow fiber membranes in sodium chloride solutions of variable concentrations (1- 4%) on the morphological and mechanical properties are the focus of this work. The results indicated variations of the dimensional parameters as compared to the untreated fibers. Thickness of all post-treated HFMs decreased showing the maximum decrease of 34% at 2% NaCl concentration. AFM testing indicated variations in the average surface roughness (Ra) manifesting an increase of 28.4% in 3% NaCl concentration and a decrease of 19.22% in 2% NaCl concentration. Moreover, assessment of observed mechanical characteristics indicated increase of break stress, break strain and tensile modulus by 8.8%, 17%, and 25.9%, respectively at 2% NaCl concentration.

Results indicated the validity of MW heating as a tuning tool for target fiber properties as intended by the subsequent use. Moreover, working in saline media confirmed contribution and interaction of water dipole rotational mechanism and ionic conduction mechanism. These results avail a reliable, efficient matrix for appropriate MW heating conditions as a possible fast and environmentally clean and reliable heating method.

Acknowledgement

This work is part of a project in the National Research Centre (NRC) entitled *"Technological and engineering development for production of desalination hollow fiber membranes.* Deep gratitude goes to the project team for their support and cooperation.

References

[1]. Peng, Na, Natalia Widjojo, Panu Sukitpaneenit, May May Teoh, G. Glenn Lipscomb, Tai Shung Chung, and Juin Yih Lai. 2012. "Evolution of Polymeric Hollow Fibers as Sustainable Technologies: Past, Present, and Future." *Progress in Polymer Science* 37 (10). Elsevier Ltd: 1401–24.

[2]. Yeo, Siek-lin, Siek-ting Yong, and Abdul Wahab Mohammad. 2015. "Post-Treatment of Polymer Membrane through Chemical and Physical Surface Modifications- A Review." *Journal of Applied Science and Agriculture* 10 (5): 104–11.

[3]. Schaub, T F, G J Kellogg, A M Mayes, R Kulasekere, J F Ankner, and H Kaiser. 1996. "Surface Modification via Chain End Segregation in Polymer Blends." *Macromolecules* 29 (11). American Chemical Society: 3982–90.

[4]. Kimihiro Mabuchi, Shiga, Noriyuki Tamamura, Shiga Osaka Hidehiko Sakurai, Shiga Noriaki Kato, and Osaka Hiroshi Shibano, Osaka Katsuhiko Nose. 2007. Bundle of selectively permeable polysulfone-based hollow fiber membranes and process for manufacturing same. US 2007/0114167 A1, issued 2007.

[5]. Mabuchi, K, H Yokota, K Kuze, N Tamamura, M Ono, N Monden, N Kato, H Shibano, and K Nose. 2007. Polysulfone-base permselective hollow fiber membrane bundle and process for producing the same. US20070187320, issued August 16, 2007.

[6]. Mabuchi, K.T.B.K.K., N.T.B.K.K. Tamamura, H.T.B.K.K. Sakurai, N.T.B.K.K. Kato, H.T.B.K.K. Shibano, and K.C.O.T.B.K.K. Nose. 2013. Polysulfone-based hollow-fiber membrane with selective permeability. EP1634610B1, issued August 28, 2013.

[7]. Yokota, H, N Kato, H Ogawa, and J Morita. 2014. Polymeric porous hollow fiber membrane. US 8881915 B2, issued November 11, 2014.

[8]. Ogawa, H, N Kato, H Yokota, and J Morita. 2012. Hollow fiber membrane for treating liquids. US8225941, issued July 24, 2012.

[9]. Mansourpanah, Y., S. S. Madaeni, A. Rahimpour, and A. Farhadian. 2009. "The Effect of Non-Contact

Heating (Microwave Irradiation) and Contact Heating (Annealing Process) on Properties and Performance of Polyethersulfone Nanofiltration Membranes." *Applied Surface Science* 255 (20): 8395–8402.

[10]. Sze Yean, Lee. 2008. "Effect of Bore Fluid and Post Treatment on Polyethersulfone Ultrafiltration Hollow Fiber Membrane." Universiti Teknologi Malaysia.

[11]. Ahmed, Iqbal, Ani Idris, Mohd Yusof Noordin, and Rizwan Rajput. 2011. "High Performance Ultrafiltration Membranes Prepared by the Application of Modified Microwave Irradiation Technique." *Industrial & Engineering Chemistry Research* 50 (4): 2272–83.

[12]. Idris, Ani, Iqbal Ahmed, and Misni Misran. 2009. "Novel High Performance Hollow Fiber Ultrafiltration Membranes Spun from LiBr Doped Solutions." *Desalination* 249 (2). Elsevier B.V.: 541–48.

[13]. Rozzi, Nicholas L, R K Singh, West Lafayette, and I I In. 2000. "The Effect of Selected Salts on the Microwave Heating of Starch Solutions" 24 (765): 265–73.

[14]. Anwar, Jamil, Umer Shafique, Waheed-uz-Zaman, Rabia Rehman, Muhammad Salman, Amara Dar, Jesus M. Anzano, Uzma Ashraf, and Saira Ashraf. 2015. "Microwave Chemistry: Effect of Ions on Dielectric Heating in Microwave Ovens." *Arabian Journal of Chemistry* 8 (1). King Saud University: 100–104.