Influence of macromolecular additives on mechanical properties of polyether sulfone and polysulfone ultrafiltration membranes

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ABSTRACT

The influence of macromolecular additives on the mechanical properties of polyethersulfone (PES) and polysulfone (PS) is investigated. Ultrafiltration membrane sheets are prepared from PES and PSF based polymers via liquid non-solvent induced phase separation (NIPS), and employing polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and Pluronic®(PLU) co-polymers as macromolecular additives. The impact of additives on the main membranes' characteristics are studied; i.e., pure water permeability, membrane porosity, morphology and surface chemistry. The main mechanical properties are examined for all membranes and are correlated to the chemical composition of the membranes. Overall, the membranes prepared using PLU showed a superior tensile strength compared to other membrane samples, while PVP was found to enhance the membrane formation by suppressing microvoids formation. This study provides a better understanding of the main mechanical and other characteristics of membrane materials with regards to using additives.

Keywords: Ultrafiltration membrane; Polyethersulfone; Mechanical properties; Tensile strength

1. Introduction

Chemical and engineering communities are paying great attention to membrane synthesis and related properties for technical applications with a positive environmental impact [1,2]. Loeb and Souriajan developed the "non-solvent-induced phase separation (NIPS)" technique and later on developed [3] asymmetric membranes with a top selective layer that helps to control separation processes supported by a porous solid matrix working as mechanical support [4]. Polysulfone (PS) and polyethersulfone (PES) are common base polymers that are broadly used to produce polymeric membranes of different pore structures and morphologies, with good chemical and thermal resistances for various applications [5,6].

Susanto et al. used modifying agents (additives) as one of several approaches to enhance characteristics of PES membranes [7]. Many studies confirm that membrane properties can be improved by introducing a second polymer like polyvinylpyrrolidone (PVP) in the casting solution, where it produces a highly porous membrane with well-interconnected pores and surface structure [5,8,9]. Moreover, PVP has the ability to increase the total polymer concentration in a casting solution by reducing the polymeric hydrodynamic size with pores distributed in binodal Gaussian

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distributions [10]. Miyano et al. emphasized that PVP works as surfactant, which increases the contact between polymer and water as gelation medium [10]. In parallel, PVP is found to increase the membrane permeability and decrease the formation of surface defects [7].

The use of polyethylene glycol (PEG) as an additive is investigated, and reported to increase the casting solution viscosity, enhance pore interconnectivity and promote the membrane surface hydrophilicity [11]. This improving effect is found to correlate with the PEG concentration and molar mass [7].

Futhermore, Pluronic®(PLU) additives shows higher surface stability levels and introduced a more hydrophilic character to PES membranes compared to PVP and PEG [12]. PLU is found to exhibit a positive impact on the bulk properties of films, including water absorption, elongation and tensile strength [13]. PLU also improves water flux and fouling resistance as reported by Susanto et al. [7] and Wang [14].

Membrane mechanical characteristics are evaluated in order to configure the effect of different polymer blends on the membrane stability under stress. Idrisa et al. report a decrease in the mechanical strength for PES membranes prepared using PEG 400 and 600 relative to PEG 200, which emphasizes the effect of modifying agents' molecular weights on membrane mechanical properties [11]. In addition, they show the effect of PEG concentration on PES membrane morphology based on scanning electron microscopy (SEM) analysis, where changing the concentration is found to reduce microvoids formation and create a very thin skin layer [11]. The variation in mechanical behavior in terms of stress strain curves in relation with structure and physical properties of electro-spun PVDF-based membranes and casting membranes is also reported [15].

Sivakumar et al. describe a strong relationship between the concentrations of casting solutions and membrane characteristics [8]. It is found that adding different amounts of PVP (0–6 wt.%) to PES membranes along with adjusting the coagulation bath temperature has remarkable impact on the membrane mechanical properties, mainly tensile strength [16]. Furthermore, it is reported that PES membranes with 1 wt% of PVP exhibit good tensile strength and elongation results compared to PES membranes containing (3, 6 and 9 wt%) PVP [9]. On one hand, this is correlated to the solubility of PVP in water, which is implied to contribute to the macrovoids formation [17]. On the other, the membranes formed by PES only show higher tensile strength. In parallel, the increase of PES percentage from 15 to 20 wt% is found to enhance the mechanical properties [9].

While the relation between membrane specifications and performance are intricate, more characterizations for membranes are still required to help for recognition of its fundamental behavior and gives a better understanding for the integration of membrane different parameters [18]. Accordingly in the current study, mechanical properties, maximum force, maximum stress and break strain for different PES and PS flat membranes prepared via NIPS and incorporating different weight percentages of PEG, PVP and PLU are investigated. Moreover, the impact of these macromolecular additives on the main membrane characteristics is studied.

2. Experimental

2.1. Materials

The following chemicals are used as purchased without further purification: PES (Utlrason- E6020P), PS (Polysulfone- Aldrich – average Mn-22,000 by MO, beads), PVP (Fluka – Polyvinylpyrrolidone, K30, average Mw 40,000), PEG (Oxford – Polyethylene Glycol 400) and PLU (Muster-Pluronic –PE 6400); Ethyl-Alcohol (96%); In addition to NMP (Emplura – 1-Methyl-2-pyrrolidone, 98%) is used as a solvent.

2.2. Membrane preparation

PES and PS are the basic polymeric materials in addition to three different additives PVP, PEG and PLU are used to fabricate flat asymmetric membrane sheets. Fourteen samples of different components and additives' concentrations are proposed to get a clear comparative study. For each modifying agent, two weight percentages, 6% and 12% are used. The following table sums up the sample combinations (Table 1).

The dope solutions are prepared according to the proposed proportions in Table 1, and they are kept under constant stirring at 300 rpm at room temperature till a clear viscous solution is attained. The solution containers are well sealed to keep constant moisture content. The prepared homogeneous solutions are cast using NIPS [19] by means of a casting machine (Model: ERICHSEN – COATMASTER 510 – 2010 – Germany, as shown Fig. 1) in order to perform a uniform thickness over the casted film at a constant casting speed of 5 mm/s. An ERICHSEN casting knife with a 200 μm clearance gap is used.

The casted films are then totally immersed in a coagulation bath containing distilled water, forming membrane white sheets at room temperature. Gentle immersion of plates prevents water turbulence and leads to a uniform surface structure. Changing the distilled water after 1 h of immersion increases the precipitation rates. Thereafter, they are kept for 24 h for complete precipitation. Plates and knives are well cleaned using towels partially immersed in ethyl alcohol (96%) to remove any fine particles that might affect sheet production.

2.3. Membrane characterization

2.3.1. Porosity

For the porosity measurements, the samples are prepared using a circular custom tool to have uniform circular samples with a diameter of 5.9 cm. The samples are dried in an oven for 30 min at 60°C to make sure that all samples are at the same conditions before measuring the dry weight and thickness. Micrometer is used to measure the samples average thickness. The porosity is then calculated by using the following formula (density method):

$$Pr = \left(1 - \frac{W}{A*d*\rho}\right) \times 100 \qquad (1)$$

Table 1
List of samples and code used

Sample code		Weight (g)					Total weight
		Main Polymer	Additive		Solvent		
1	PES-B-01		Blank	0		42.5	
2	PES-V6-01		PVP	3		39.5	
3	PES-V12-01			6		36.5	
4	PES-E6-01	PES 7.5	PEG	3	NMP	39.5	
5	PES-E12-01			6		36.5	
6	PES-L6-01		PLU	3		39.5	
7	PES-L12-01			6		36.5	50 g
8	PS-B-01		Blank	0		42.5	
9	PS-V6-01		PVP	3		36.5	
10	PS-V12-01			6		39.5	
11	PS-E6-01	PS 7.5	PEG	3	NMP	36.5	
12	PS-E12-01			6		39.5	
13	PS-L6-01		PLU	3		36.5	
14	PS-L12-01			6		39.5	

Sample Code Legend

Sample number of trials

Additive Concentration Indication:
6 for 6%
12 for 12%

PES-V6-01

Main Polymer

Additive Indication:
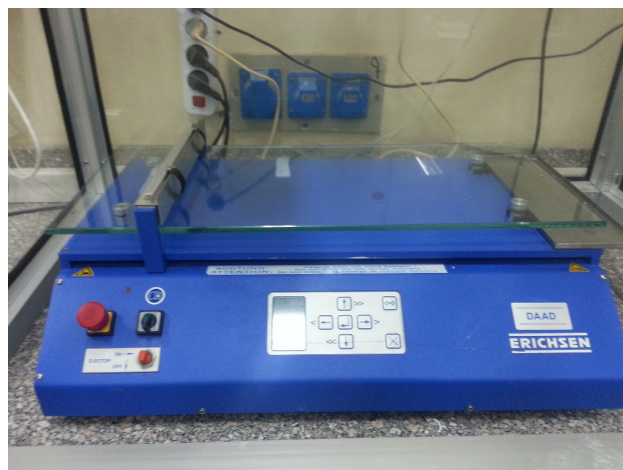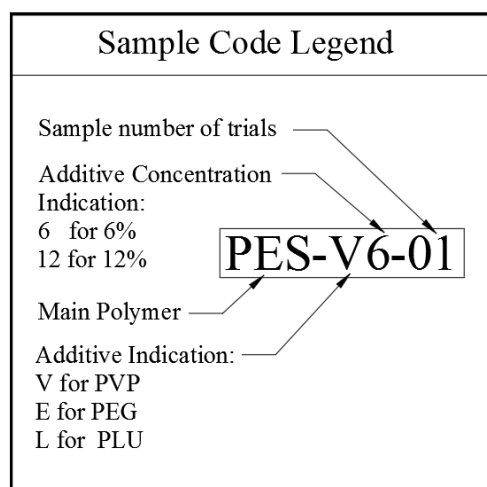V for PVP
E for PEG
L for PLU

Fig. 1. COATMASTER casting machine.

where W is the dry weight in g, A is the sample area in cm², d is the thickness in cm and ρ is the sample density in g/cm³. Assuming solvent /NMP totally precipitated, the sample density is approximately equal to the main polymer density (PES, 1.37 g/c.c.).

The swelling method is a different way to measure porosity using wet weight in addition to dry weight. The samples are immersed in ethanol for 1 h, then in water for 3 h to achieve full wettability. Then, the wet samples are weighed. The following formula is used for calculations:

$$\epsilon = \left(\frac{w_1 - w_2}{A * L * d_w} \right) \times 100 \qquad (2)$$

where w_1 is the wet weight in g, w_2 is the dry weight in g, A is sample area in cm², L is thickness in cm and d_w is the water density in g/cm³.

2.3.2. Surface chemistry

The membrane surface chemistry is analyzed by using Fourier transform infrared spectroscopy (FTIR) Excalibur series (ThermoScientific, USA). All samples are tested at room temperature (25°C).

2.3.3. Permeability studies

The permeability studies are performed as an analytical tool for compacted membranes subjected to pure water flux (PWF) and defined pressure. Calculations are done using the equations given below, which are based on counting the amount of PWF passing through membrane samples versus the time consumed [20]. Experiments are carried out using dead-end filtration cell where in normal conditions pure water flows through membranes under a pressure range of 2–3 bar for around 3 min. Then membranes are compacted by increasing applied pressure to 5 bar for 30 min, Afterward, the pressure is reduced again and the membranes are re-tested in normal conditions to check the flow behavior after compaction.

The experimental cell used for permeability testing is presented schematically in the Fig. 2, which is comprised of (1) pressure source- nitrogen cells, (2) feed tank, (3) pressure unit, (4) flux collector unit.

The membrane samples are placed perpendicular to the water flow direction [20]. PWF (L/m²h) is calculated as a relation of water volume permeated through the membrane sample V (L) relative to the effective membrane area A (m²) and permeation time ΔT (h), according to the following equation: [20]

$$\text{PWF} = J_W = F = \frac{V}{A \times \Delta T} \qquad (3)$$

where PWF values differ based on the applied pressure range. Hydraulic permeability P_m (L/m²h·bar) is calculated via normalizing J_w by the applied trans-membrane pressure ΔP (bar) [20].
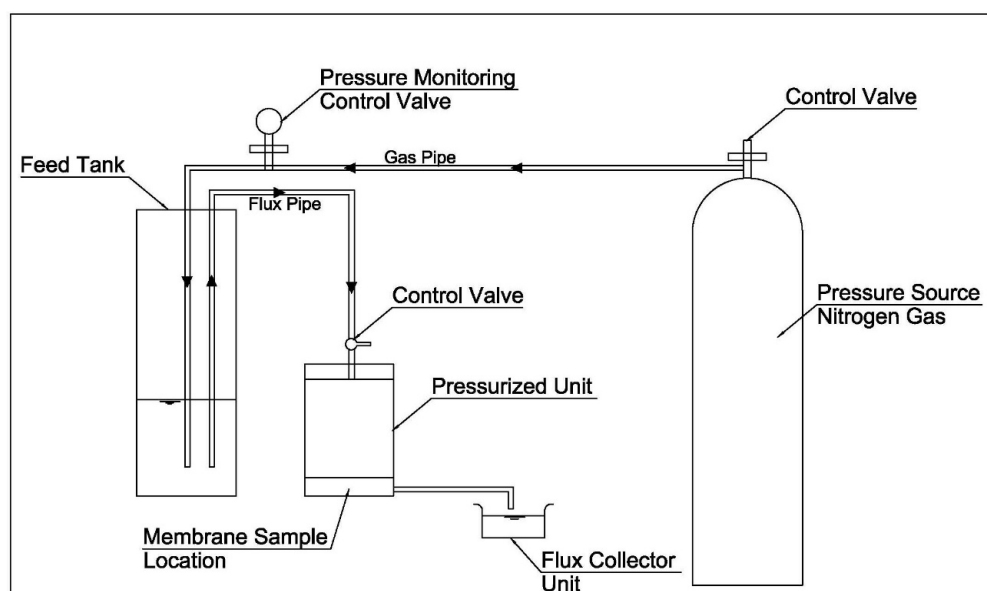
$$P_m = \frac{J_w}{\Delta P} \qquad (4)$$

Fig. 2. Sketch of the permeability experimental cell used.

2.3.4. Scanning electron microscopy (SEM)

The surface and cross sectional morphology of the membranes is analyzed using a Quanta 400 FEG environmental scanning electron microscope (ESEM;FEI) at standard high vacuum conditions. AK-550 sputter coater (Emitech, U.K.) is used to coat the outer surface of the sample with gold for both top and cross section. Sputtering is done for 5.0 min.

2.3.5. Mechanical studies

The mechanical properties are studied using a tensile testing machine (Model: Shimadzu, Load Cell, Type: Slfl-100kn). The tension test is performed by fixing sample edges from both sides and applying linear increasing force in order to record the breakdown point. For each sample the values of the maximum applied force, maximum resulting stress and breaking strain are determined for one time.

Where stress (ρ) is defined as the ratio between applied axial load/force and sample cross-sectional area and strain represents the percentage of sample elongation under stress forces [21].

$$\rho = \frac{F}{A} \tag{5}$$

All calculations are done based on the samples' standard dimensions. A secondary sampling tool (Model: Zwick/Roell, Bzcp020) is used to cut samples. A micrometer is used to measure the sample thickness. Fig. 3 shows a sketch for the tensile machine and standard sample shape.

3. Results and discussions

3.1. Effect of membrane compositions on surface properties

Fourier transform infrared (FTIR) is used as a tool to investigate how the change in the chemical composition of
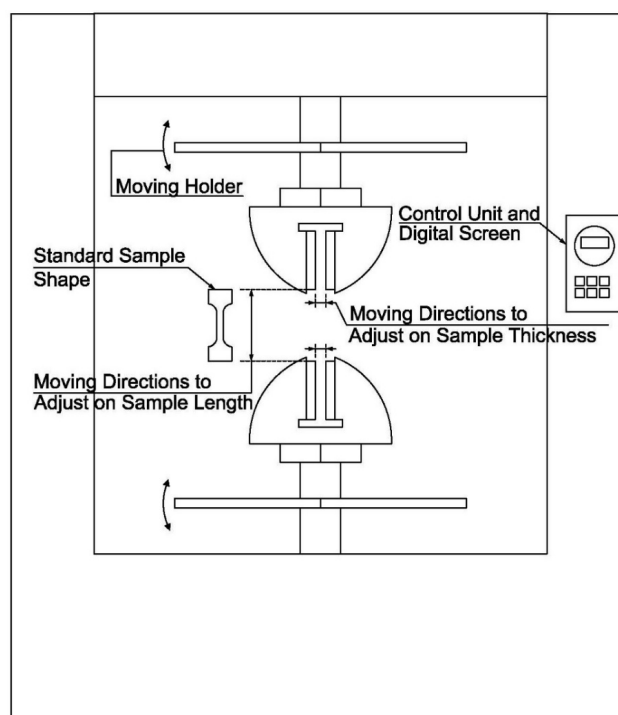

Fig. 3. Sketch of the tensile machine used.

the membranes reflects on surface properties. As shown in (Fig. 4), samples 1–7 show common peaks at –1503 to –1268 cm^{-1} assigned to C=C bond, benzene ring and the aromatic ether bond as typical spectra for PES [7,12]. It's hard to compare their IR spectra because PES peaks are very strong and overlap with other additives patterns, that comes in line with other studies [22]. Minor peaks due to additives with different concentration are found in the range of 752
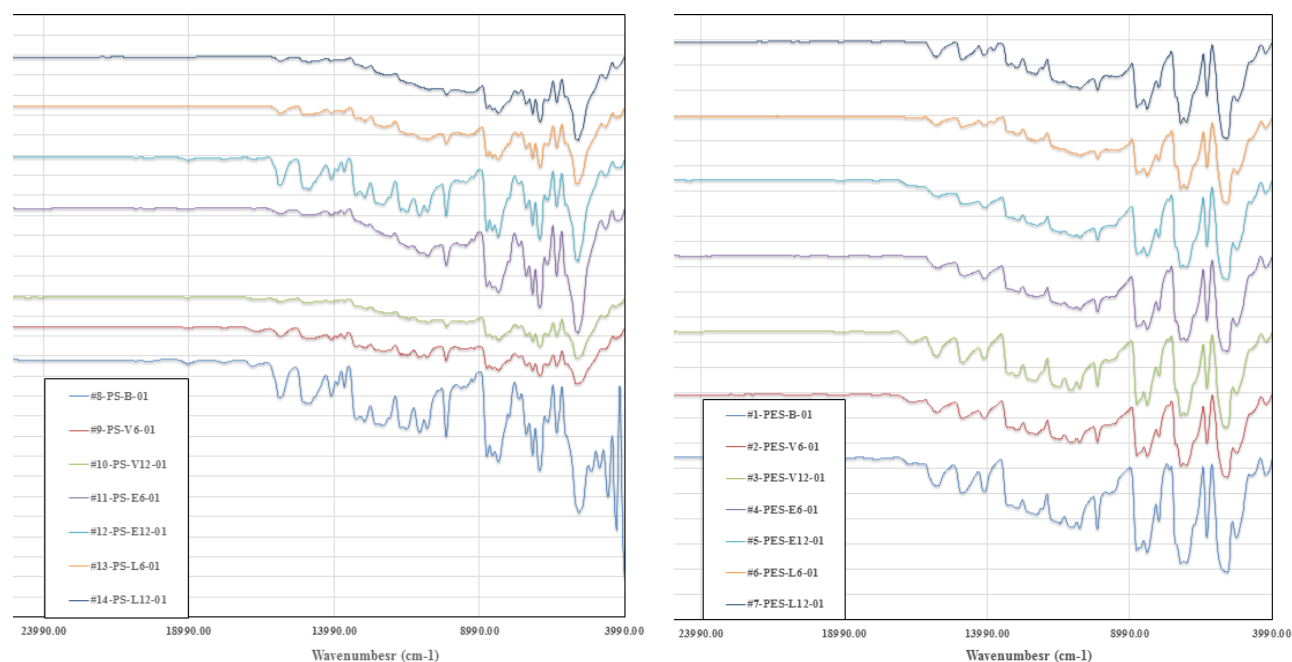
Fig. 4. FTIR spectra for the membrane samples under investigation.

Table 2
Porosity test results of the membranes under investigation

| Sample code | | Compositions (wt. %) | | | | | | Porosity (%) | |
		PES	PS	PVP	PEG	PLU	NMP	Density method	Swelling method
1	PES-B-01	15	–	–	–	–	85	79.2	54.9
2	PES-V6-01	15	–	6	–	–	79	86.0	80.2
3	PES-V12-01	15	–	12	–	–	73	81.9	144.0
4	PES-E6-01	15	–	–	6	–	79	79.5	22.3
5	PES-E12-01	15	–	–	12	–	73	80.8	34.9
6	PES-L6-01	15	–	–	–	6	79	85.2	85.6
7	PES-L12-01	15	–	–	–	12	73	35.5	28.2
8	PS-B-01	–	15	–	–	–	85	69.8	84.9
9	PS-V6-01	–	15	6	–	–	79	41.5	79.1
10	PS-V12-01	–	15	12	–	–	73	70.3	121.5
11	PS-E6-01	–	15	–	6	–	79	83.4	75.6
12	PS-E12-01	–	15	–	12	–	73	84.6	78.7
13	PS-L6-01	–	15	–	–	6	79	88.0	86.4
14	PS-L12-01	–	15	–	–	12	73	88.8	86.8

and 607 cm^{-1} and are partly overlapping with bands of PES [7,12].

On the other hand membrane samples prepared from polysulfone as a main polymer (samples 8–14) show a different pattern having the base polymer PS at aromatic frequencies of ~858 to ~1268 cm^{-1} [23]. The spectrum of the blank PS membrane (Sample 8) a very rapid pattern with the main peaks at 1577 cm^{-1}, 1484 cm^{-1}, 1294 cm^{-1} and 1012 cm^{-1}, which are the characteristics of aromatic C-H stretch, C-O-C stretch, S=O stretch and C-C aromatic frequencies, respectively [24].

3.2. Effect of membrane compositions on pore structures

To assess the effect of membrane composition on pore structures, the membrane porosity is tested for the samples fabricated with different polymers (PES and PS), additive

types (PVP, PEG and PLU) and concentrations (6% and 12%) as shown in Table 2. It is apparent that the combinations of PVP/PES and PLU/PS show the highest porosity among all other combinations with density and swelling values around 80–144%. A faster phase separation rate is attributed to the effect of PVP on solution viscosity as a result of the interaction between polymer and solvent as well as casting solutions with PVP additive [7]. Yoo et al. compare morphologies of various cross-sectional asymmetric membranes with various PVP concentrations. It is found that macrovoid formation is suppressed by adding PVP to the casting solution [25]. Other supporting studies explain how PVP works against macrovoid formation by minimizing the possibility of delayed demixing and enhancing pore interconnectivity, which ensure better porosities inside both top and sub layers. This results in an increase in pure water permeation (PWP) [26]. On the other hand, studies show Pluronic addition effects on membrane structures at various Pluronic concentrations. This lies in good accord with our findings and explains the increase in density or swelling porosity test values [27]. Other factors influencing the addition to Pluronic tendency for increasing membrane porosity [28] is the compatibility between polysulfone as hydrophobic polymer and Pluronic different segments. Pluronic PEO (poly ethylene oxide) segments enrich the membrane surface with higher hydrophicility while Pluronic-PPO (propylene oxide) segments ensure well polymer matrix anchoring [29].

3.3. Effect of membrane compositions on permeability analysis

Applying pressure to membranes prepared using PLU during the permeability tests result in higher flux behavior as shown in Fig. 4 and Fig. 5 featuring before and after compaction results. Excellent behavior of PES/PLU samples "PES-L6-01" and "PES-L12-01" shown in Figs. 5, 6 with flow/pressure values for before and after compaction 1.67 to 1.20, respectively, for the first sample and 0.8 to 0.53, respectively, for the second one, can be explained as densification of a porous support layer forming more thickening skin layer that works as selective barrier [7]. Moreover, it is shown that while increasing the Pluronic concentration, top layer thickness decreased and the volume of porous sub layer increased [27]. Consequently, in line with other studies [7], compaction resulted in thickening of membrane selective layers showing low flux permeability performance. This explains behavior of PVP or PEG membranes as in samples "PES-V6-01" and "PS-E6-01". The unexpected behavior of sample "PES-E6-01" after compaction by having no flux at all could be linked to pore blocking defect in sample casting more than any chemical effect.

3.5. Effect of membrane compositions on mechanical properties

In this study, membrane mechanical analysis is represented in Figs. 7 and 8 with force/strain curves as a way to check how membrane structures act under different forces based on the chemical composition.

Table 3 depicts mechanical experimental results that indicate high strain resistance for "PES-L6-01" and "PS-
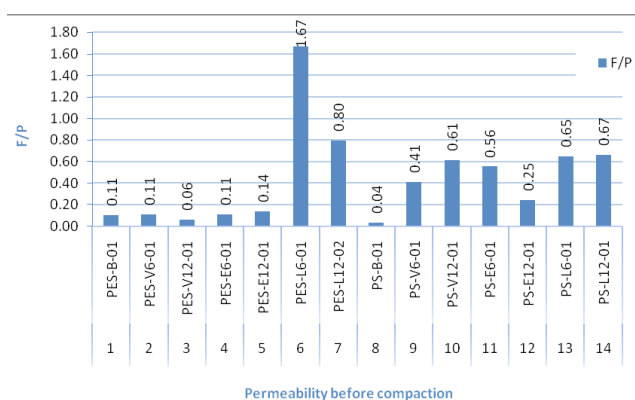

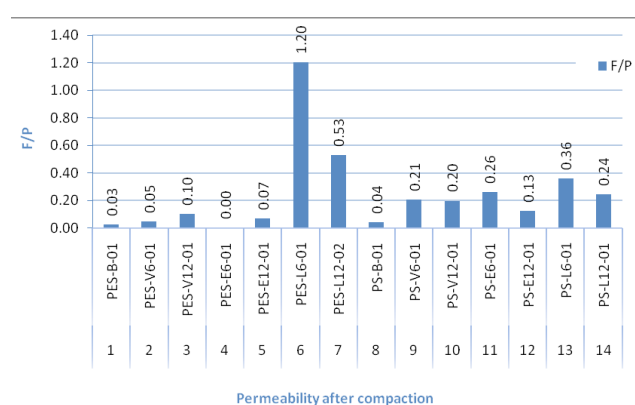Fig. 5. Permeability results before compaction.

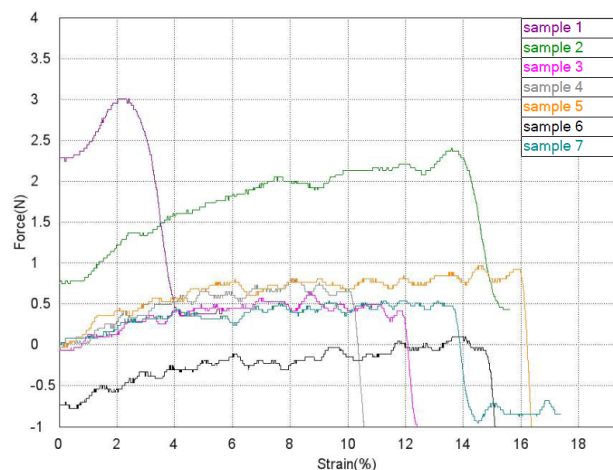Fig. 6. Permeability results after compaction.

Fig. 7. Force/Strain curves for samples 1 to 7.

L6-01" samples with values 15.2% and 16.5% respectively due to presence of PLU additive. This lies in congruence with the PLU effect in the mentioned samples. Zhao et al. followed the same procedure and reported high surface hydrophobicity and surface segregation of Pluronic molecules when introduced to PES membranes [30]. Moreover,

the same PES/PLU combination in sample "PES-L6-01" shows an excellent behavior in the previously discussed permeability results which reflects the behavior of formed porous support layer on increasing membrane mechanical strength.

Pluronic characteristics as a fouling resistance component reflected by the strength of surface is another supportive factor [31] for choosing it as an additive [32]. However other studies prove that change in filler concentration forms stress convergence points leading to weakening membrane mechanical stability [33]. The concentration negatively affects particles aggregation and makes them non-uniformly shaped in the polymer matrix which might explain grouping of spherical particles in sample "PS-L12-01-Top" SEM photo, which results in forming stress convergence points when applying outside force. Filler concentration has a peak point on strength curve which declines with further
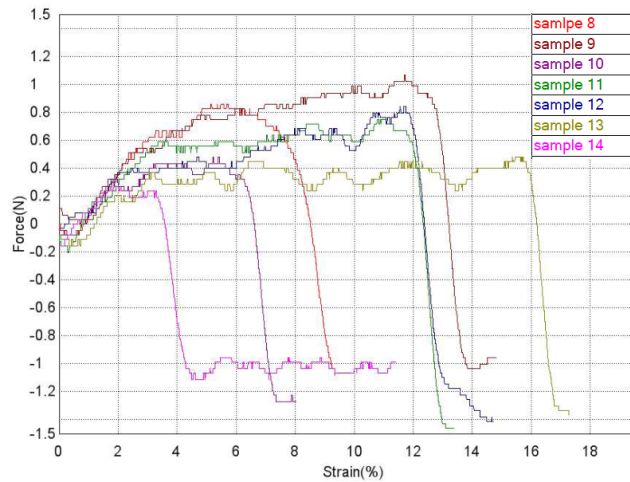
increase in concentration [33]. The surface and the cross-sectional morphologies are observed by use of a JSM-5500 LV scanning electron microscope (SEM, Japan Electron) (Fig. 9) for one of highest and lowest break strain samples: "PES-L6-01" and "PS-L12-01", to show convergence points in the sample "PS-L12-01" leading to low mechanical stability.

4. Conclusions

The dependence of selected mechanical properties of ultrafiltration membranes on type and concentration of the used chemical components during fabrication is investigated. This study clearly links the change in chemical components with different concentrations reflected on both physical and mechanical properties.

The use of PVP, PEG and PLU as different additives with low (6%) and high (12%) concentrations for PES and PS membranes creates a wide range of application possibilities with 14 membrane samples of different properties were fabricated and experimentally tested under the same conditions.

Generally, PVP shows an excellent structure forming effect among all tested samples based on pore structure analysis, while PLU shows the best results for both permeability and tensile testing.

As an important output of this study, accurate expectations for membrane behavior for different applications that are more relevant for actual working conditions of membranes become obvious.

Acknowledgement

Fig. 8. Force/Strain curves for samples 8 to 14.

Table 3
Results of mechanical tests of the membranes under investigation

	Sample code	Dimensions		Testing results		
		Thickness (mm)	Width (mm)	Max force (N)	Max stress (N/mm²)	Break strain (%)
1	PES-B-01	0.04	62	3.0	12.1	3.8
2	PES-V6-01	0.03	62	2.4	12.9	15.1
3	PES-V12-01	0.03	61	0.7	3.6	12.3
4	PES-E6-01	0.01	61	0.8	13.3	10.6
5	PES-E12-01	0.02	61	1.0	7.9	16.3
6	PES-L6-01	0.04	61	0.1	0.4	15.2
7	PES-L12-01	0.08	61	0.5	1.1	14.0
8	PS-B-01	0.03	61	0.9	4.7	8.9
9	PS-V6-01	0.06	61	1.1	2.9	13.4
10	PS-V12-01	0.03	61	0.5	2.6	7.0
11	PS-E6-01	0.05	61	0.7	2.4	12.8
12	PS-E12-01	0.07	61	0.8	2.0	12.7
13	PS-L6-01	0.08	61	0.5	1.0	16.5
14	PS-L12-01	0.06	61	0.3	0.7	4.3

a. Sample: 6-PES-L6-01 - Top

b. Sample: 14-PS-L12-01- Top

c. Sample: 6-PES-L6-01 – Cross Section

d. Sample: 14-PS-L12-01– Cross Section
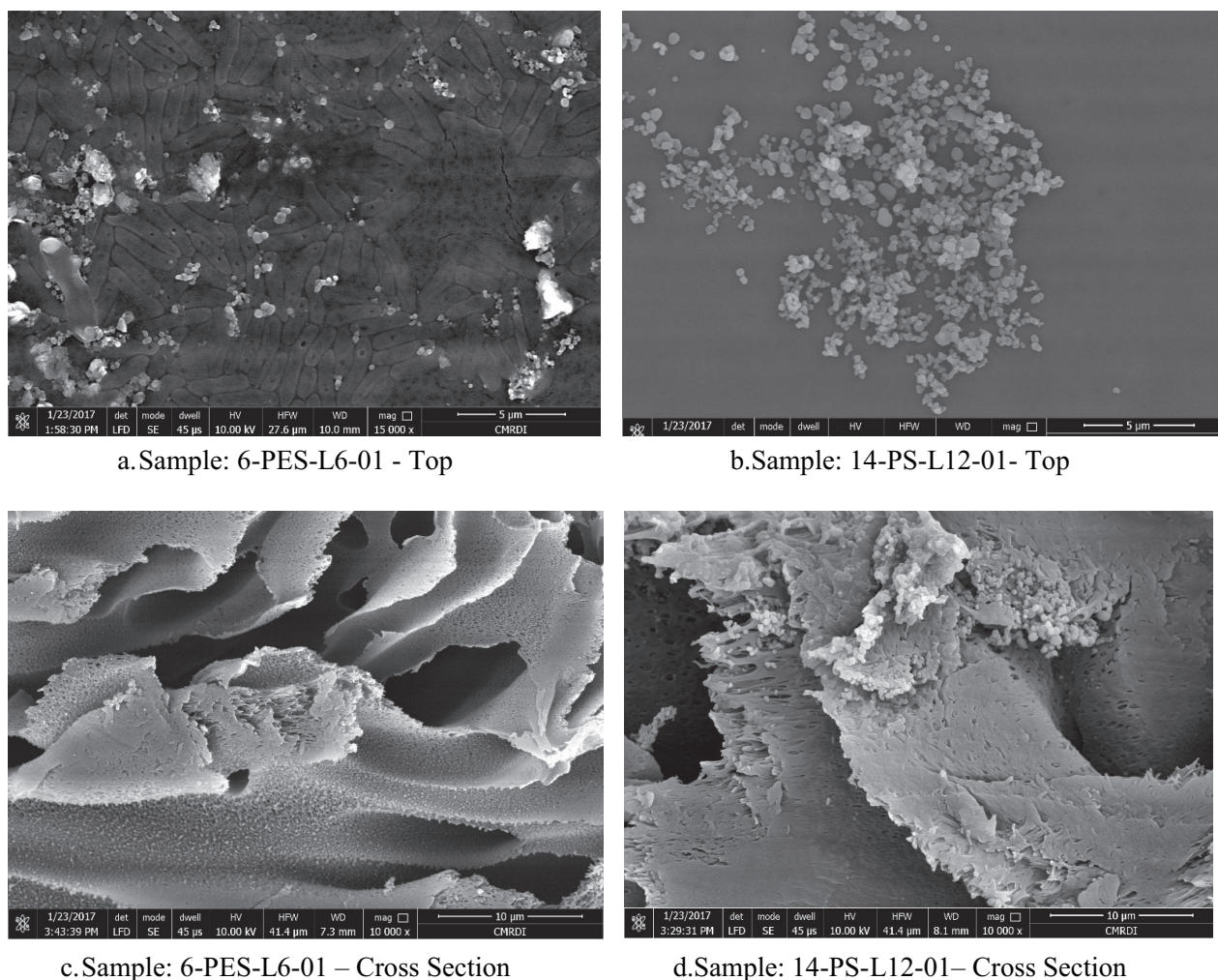
Fig. 9. SEM micrographs of selected samples.

References

[1]   E. Drioli, A. Criscuoli, E. Curcio, Membrane Contactors : Fundamentals, Applications and Potentialities, Elsevier, 2006.

[2]   M.L. Méndez, A.I. Romero, V.B. Rajal, E.F. Castro, J.I. Calvo, L. Palacio, A. Hernández, Properties of polyethersulfone ultrafiltration membranes modified with polyethylene glycols, Polym. Eng. Sci., 54 (2014) 1211–1221.

[3]   C.H. Loh, R. Wang, Effects of additives and coagulant temperature on fabrication of high performance PVDF/pluronic F127 blend hollow fiber membranes via nonsolvent induced phase separation, Chinese J. Chem. Eng., 20 (2012) 71–79.

[4]   C. Feng, R. Wang, B. Shi, G. Li, Y. Wu, Factors affecting pore structure and performance of poly(vinylidene fluoride-co-hexafluoro propylene) asymmetric porous membrane, J. Membr. Sci., 277 (2006) 55–64.

[5]   Z.-L. Xu, F. Alsalhy Qusay, Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution, J. Membr. Sci., 233 (2004) 101–111.

[6]   J. Xie, Q. Wei, B. Su, B. Qian, Q. Ling, C. Zhao, Preparation and characterization of sandwich-structure polyethersulfone membrane with pH sensitivity, Desal. Water Treat., 8 (2009) 163–170.

[7]   H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci., 327 (2009) 125–135.

[8]   M. Sivakumar, D.R. Mohan, R. Rangarajan, Studies on cellulose acetate-polysulfone ultrafiltration membranes: II. Effect of additive concentration, J. Membr. Sci., 268 (2006) 208–219.

[9]   S.A. Al Malek, M.N. Abu Seman, D. Johnson, N. Hilal, Formation and characterization of polyethersulfone membranes using different concentrations of polyvinylpyrrolidone, Desalination, 288 (2012) 31–39.

[10]   T. Miyano, T. Matsuura, S. Sourirajan, Effect of polyvinylpyrrolidone additive on the pore size and the pore size distribution of polyethersulfone (victrex) membranes, Chem. Eng. Commun., 119 (1993) 23–39.

[11]   A. Idris, N. Mat Zain, M.Y. Noordin, Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, Desalination, 207 (2007) 324–339.

[12]   H. Susanto, N. Stahra, M. Ulbricht, High performance polyethersulfone microfiltration membranes having high flux and stable hydrophilic property, J. Membr. Sci., 342 (2009) 153–164.

[13] J.H. Lee, Y.M. Ju, D. M. Kim, Platelet adhesion onto segmented polyurethane film surfaces modified by addition and cross-linking of PEO-containing block copolymers, Biomaterials, 21 (2000) 683–691.

[14] Yan-qiang Wang, Ting Wang, Yan-lei Su, Fu-bing Peng, Hong Wu, Z. Jiang, Remarkable reduction of irreversible fouling and improvement of the permeation properties of poly(ether sulfone) ultrafiltration membranes by blending with pluronic F127, Langmuir, 21 (2005) 11856–11862.

[15] K. Gao, X. Hu, C. Dai, T. Yi, Crystal structures of electrospun PVDF membranes and its separator application for rechargeable lithium metal cells, Mater. Sci. Eng. B, 131 (2006) 100–105.

[16] M. Amirilargani, E. Saljoughi, T. Mohammadi, M.R. Moghbeli, Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes, Polym. Eng. Sci., 50 (2010) 885–893.

[17] I. Cabasso, E. Klein, J.K. Smith, Polysulfone hollow fibers. I. Spinning and properties, J. Appl. Polym. Sci., 20 (1976) 2377–2394.

[18] S.C.A. Cuperus F.P., Characterization of UF membranes: Membrane characteristics and characterization techniques, Adv. Colloid Interface Sci., 34 (1991) 135–173.

[19] W. Partlow, The Nature of Synthetic Membranes, Chemical Engineering, 2016, 1–3.

[20] K.A. Gebru, C. Das, Effects of solubility parameter differences among PEG, PVP and CA on the preparation of ultrafiltration membranes: Impacts of solvents and additives on morphology, permeability and fouling performances, Chinese J. Chem. Eng., 2017.

[21] K. Khanafer, A. Duprey, M. Schlicht, R. Berguer, Effects of strain rate, mixing ratio, and stress–strain definition on the mechanical behavior of the polydimethylsiloxane (PDMS) material as related to its biological applications, Biomed. Microdevices, 11 (2009) 503–508.

[22] C.H. Loh, R. Wang, L. Shi, A.G. Fane, Fabrication of high performance polyethersulfone UF hollow fiber membranes using amphiphilic Pluronic block copolymers as pore-forming additives, J. Membr. Sci., 380 (2011) 114–123.

[23] A. Pagidi, R. Saranya, G. Arthanareeswaran, A.F. Ismail, T. Matsuura, Enhanced oil–water separation using polysulfone membranes modified with polymeric additives, Desalination, 344 (2014) 280–288.

[24] S.B. Teli, A. Benamor, M. Nasser, A. Hawari, S.J. Zaidi, M. Ba-abbad, A.-W. Mohammad, Effects of amphiphilic pluronic F127 on the performance of PS/SPEEK blend ultrafiltration membrane: Characterization and antifouling study, J. Water Process Eng., 18 (2017) 176–184.

[25] S.H. Yoo, J.H. Kim, J.Y. Jho, J. Won, Y.S. Kang, Influence of the addition of PVP on the morphology of asymmetric polyimide phase inversion membranes: effect of PVP molecular weight, J. Membr. Sci., 236 (2004) 203–207.

[26] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive, J. Membr. Sci., 315 (2008) 36–47.

[27] C. Lv, Y. Su, Y. Wang, X. Ma, Q. Sun, Z. Jiang, Enhanced permeation performance of cellulose acetate ultrafiltration membrane by incorporation of Pluronic F127, J. Membr. Sci., 294 (2007) 68–74.

[28] A. Venault, Y. Chang, Surface hydrophilicity and morphology control of anti-biofouling polysulfone membranes via vapor-induced phase separation processing, J. Nanosci. Nanotechnol., 13 (2013) 2656–2666.

[29] R. Raslan, A. Mohammad, Polysulfone/pluronic F127 blend ultrafiltration membranes: preparation and characterizations, J. Appl. Sci., 10 (2010) 2628–2632.

[30] W. Zhao, Y. Su, C. Li, Q. Shi, X. Ning, Z. Jiang, Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent, J. Membr. Sci., 318 (2008) 405–412.

[31] Y.-Q. Wang, Y.-L. Su, X.-L. Ma, Q. Sun, Z.-Y. Jiang, Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance, J. Membr. Sci., 283 (2006) 440–447.

[32] F. Meng, S.-R. Chae, A. Drews, M. Kraume, H.-S. Shin, F. Yang, Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material, Water Res., 43 (2009) 1489–1512.

[33] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO$_2$ fillers on the morphologies and properties of PSF UF membrane, J. Membr. Sci., 288 (2007) 231–238.