

COMBINED MECHANICAL FIELDS

TENSILE AND SURFACE MECHANICAL PROPERTIES OF
POLYETHERSULPHONE (PES) AND POLYVINYLIDENE
FLUORIDE (PVDF) MEMBRANES

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ABSTRACT: Mechanical properties of polymer membranes (strength, hardness and elasticity) are very important parameters for the application performance, e.g. water purification. We study the tensile and surface mechanical properties of hollow fiber and flat sheets mat membranes based on PES and PVDF polymers. Tensile test, nanoindentation and atom force microscopy are used for characterization at macro and nanoscale. Mechanical properties are correlated with pore structure of membranes. The reinforced PVDF HF hollow fiber membranes show 30-fold higher stiffness and 3-fold higher hardness compared to non-reinforced PES HF. Surface mechanical properties of flat sheet membranes are strongly improved by decreasing the pore size. The smoothest surface with 100–200 nm roughness has the best surface mechanical performance obtained by nanoindentation.

KEY WORDS: membranes, mechanical properties, tensile strength, nanoindentation, atom force microscopy, structure-property relation.

1 INTRODUCTION

Water is an invaluable vital natural resource for human life. Currently, the world is undergoing a critical water quality crisis because of the increasing number of populations, poor practices of industrialization and urbanization, as well as the uncontrollable discharge of polluted and harmful water. However almost one billion people in the world do not have ready access to safe drinking water and over 3.6 million people around the world die each year from drinking unsafe water [1, 2]. A broad range of water treatment technologies are available/been used for wastewater recycling and for purification of drinking water. Physical water treatment, membrane-based processes have received significantly increased interest over the last few decades.

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A membrane is a layer of material which serves as a selective barrier (filter) between two phases and some components are allowed passage by the membrane into a permeate stream, whereas others remains impermeable, depending on their physical and chemical properties [1]. The driving force for the separation process is the pressure difference between the feed and permeate side, the so-called transmembrane pressure [2]. The selectivity of the membrane is a function of its pore size, the diffusivity within the matrix and the associated electrostatic charges [1–3]. The membrane separation processes are categorized into four classes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis [2]. The first two are low pressure processes while the last two are high pressure processes. Materials removed by MF include sand, silt, clays, suspended solids, cysts, algae, and some bacterial species. Ultrafiltration provides an absolute barrier to almost all microbiological species as bacteria and viruses, nanoparticles, high molecular weight organic molecules, most proteins, emulsified oils and colloids [3].

A number of different materials are used to prepare membranes for use in water treatment. These materials can be broadly classified as either organic (polymer membranes) or inorganic (ceramic membranes). Polyvinylidene fluoride (PVDF) and polyethersulfone (PES) are widely used materials in separation fields, especially in the field of water purification and have recently received great attention as membrane materials with regard to their outstanding properties, such as high mechanical strength, excellent chemical resistance and thermal stability [4,5].

Flat sheet porous polymeric membranes can be fabricated by several methods, including sintering, stretching, track etching, and phase separation processes [5]. Hollow fiber membranes are specific type membranes, that may operate in an “inside-out” or “outside-in” mode [1,6]. In inside-out mode, feed water enters the center of the fiber (lumen) and is filtered radially through the fiber wall. Filtrate is then collected from outside the fiber. During outside-in operation, feed water passes from outside the fiber to the inside, where filtrate is collected in the center of the fiber. Recent studies have investigated the possibility of coupling membrane filtration and a photo catalyst, because of interesting property of these membranes to mitigate membrane fouling. Among photocatalysts, anatase-type titanium dioxide (TiO_2) presents several advantages: an important photocatalysis activity under UV irradiation, a high stability and low environmental impact [7].

The mechanical properties of polymer membranes (% elongation, tensile strength, hardness) determine their application [8] and this make a strength very important parameter. It has been shown that morphological parameters such as pore size and pore architecture have a major effect on the properties of polymeric membranes because if pore size increased, a mechanical strength decreased [9,10]. Identifying the failure mechanisms that govern fracture can lead to more optimized architectures, to find

optimum membrane pore size to better mechanical performance. A decrease in the tensile strength with pore enlargement is usually due to the decrease in surface area of the membrane [10].

The aim of this study was to create innovative PES and PVDF membranes, both hollow fibers and flat sheets, as varying the pore size with the latest membrane morphology and to characterize their bulk and surface mechanical properties. Innovative nano-photocatalytic membranes were fabricated at Jadavpur University by using unique spinning technology for producing hollow membranes. Flat sheet membranes were also fabricated from the same materials by film casting techniques [11]. The mechanical properties were characterized in this study and correlated with the pore structure of the membranes in order to estimate their performance for some application needs.

2 EXPERIMENTAL

2.1 MATERIALS

Two types of membranes have been characterized in this study: hollow fiber membrane and flat sheet mat. The hollow fiber membranes were based on polyethersulfone (PES HF) and polyvinylidene difluoride (PVDF HF) polymers, widely used for

Table 1. Type and characteristics of membranes used in this study

No	Name	Average pore size, μm	Thickness, μm	Membrane type
1	PES HF	0.03–0.14	$D = 2 \text{ mm}$ $L = 15 \text{ mm}$	Polyethersulfone hollow fiber membrane
2	PVDF HF	0.02–0.4	$D = 2 \text{ mm}$ $L = 15 \text{ mm}$	Polyvinylidene difluoride hollow fiber membrane
3	PVDF 0.08M	0.08	130–185	Polyvinylidene difluoride membrane of pore size $0.08 \mu\text{m}$; Flat sheet mat membrane
4	PVDF 50000 UF	0.02	80–140	Polyvinylidene difluoride membrane of MWCO* 50,000 Dalton; Flat sheet mat membrane
5	PVDF 100000	0.01	90–100	Polyvinylidene difluoride membrane of MWCO* 100,000 Dalton; Flat sheet mat membrane

(*) Molecular weight cut-off (MWCO) refers to the lowest molecular weight solute (in daltons) in which 90% of the solute is retained by the membrane.

membrane preparation. The flat sheet mat membranes were based on polyvinylidene difluoride (PVDF) polymer of different molecular weight. Table 1 summarizes the type of membranes studied.

The membrane characteristics in Table 1 were determined in the Jadavpur University. The pore size and MWCO of membranes were tested by a permeation of a mixture of polyethylene glycols, with a broad molecular weight (MW) range, in a standardized cell, where the pressure and cross flow velocity was controlled in order to create standard conditions for the measurements. After the permeation experiment is carried out, the MW distributions of feed and permeate are determined using Gel Permeation Chromatography (GPC). The molecular weight where the rejection is 90% was verified.

2.2 MEMBRANE PROCESSING AND FABRICATION

The membranes were fabricated in Jadavpur University, India by using the following techniques:

2.2.1 PREPARATION OF HOLLOW FIBER MEMBRANES

Hollow fiber membranes were prepared by a batchtype extruder. The homogeneous polymer solution based on PES and PVDF was fed to a spinneret by a gear pump under the pressure of nitrogen. The spinneret consists of outer and inner tubes. The diluent was introduced into the inner orifice to make a lumen of the hollow fiber. The hollow fiber was extruded from the spinneret and wound on a take-up winder after entering into a bath kept the temperature to induce the phase separation and solidify the membrane. The extrusion rate of the polymer solution and the flow rate of the diluent in the inner tube of the spinneret were fixed at 0.075 and 0.497 m/s, respectively. The diluent remaining in the hollow fiber membrane was extracted by immersing them into water. The PVDF membrane was reinforced by a cotton fiber inserted in the inner orifice (Fig. 1).



Fig. 1. (Color online) Visualization of hollow membranes (left) and flat sheet membrane (right).

2.2.2 PREPARATION OF FLAT SHEET MEMBRANES

Microporous PES membrane casting : Polyethersulfone (PES) was used as polymer for membrane casting. Analytical grade N-N dimethylformamide (DMF) of $M = 73$ g/mol was purchased from Merck Germany. Polyethersulfone was dried in an oven at a temperature of 80°C for 24 hours to remove any moisture present in it. Dope solution was prepared by dissolving fixed 15 wt% of polyethersulfone in solvent N-N dimethylformamide with constant stirring for 7–8 hours. The dope solution was poured onto a clean glass plate at room temperature and casted on a glass plate using a casting knife. Immediately after casting, the glass plate with the casted film was dipped into reverse osmosis water at room temperature. After few minutes, a thin polymeric film separated out from the glass plate due to the phase inversion process. The membrane was washed with distilled water and transferred to another container ready to be tested.

PVDF asymmetric flat membrane casting : The homogeneous PVDF casting solutions were prepared at 60°C, at room temperature, and the standing time of the casting solution was at least 24 h to eliminate the bubbles inside. The casting solutions were cast onto a glass plate at 25°C and 60% relative humidity by means of a glass rod, and then were immersed into a coagulation bath (deionized water at 25°C), immediately. The pristine membranes were kept in fresh water for 1 week, and the deionized water was changed twice one day to ensure complete removal of the residual solvent from the membranes.

2.3 EXPERIMENTAL METHODS FOR CHARACTERIZATION

2.3.1 TENSILE STRENGTH MEASUREMENTS

The tensile tests of the fabricated hollow fiber membranes, PVDF and PES, were carried out using a Universal Mechanical and Tribological Tester UMT-2M (Bruker) at room temperature. The samples were clamped at both ends and pulled at constant elongation velocity of 0.1 mm/sec. Ultimate Tensile strength, Yield strength, Young's modulus, Elongation at Ultimate strength, Toughness, Energy at Yield point were obtained. Ten tube (circular-shaped) samples with gauge dimensions of 15 mm in length and 2 mm in diameter were tested for each hollow fiber membrane. A displacement has been applied to each test piece until a failure of the sample. The flat sheet membranes were with very low thickness, and the reason for not being measured was the lack suitable grip and force sensor.

2.3.2 NANOINDENTATION MEASUREMENTS

Nanomechanical fine analyses are performed using Universal Nanomechanical Tester (UNMT, Bruker), equipped with Nanoindenter & Atomic Force Microscopy (AFM, Ambios Technology). Flat sheet membranes were tested. For each specimen 24 nano-indentations were made with maximum force applied of 5mN. The 70 nm diamond-tip Berkovich indenter was used to perform the tests and specialized software to calculate the hardness and the modulus of elasticity of the specimens using the Oliver-Pharr method [12]. Loading procedure for all specimens: 1) Uniform loading from 0 to maximum load of 5 mN for 15 s; 2) 10 s holding of maximum load of 5 mN; 3) 15 s unloading to 10% of maximum loading – 0.5 mN; 4) 15 s holding of 10% of maximum loading – 0.5 mN; 5) Total unloading for 1 s. All nano-indentation tests were performed at constant temperature 20°C.

2.3.3 AFM MEASUREMENTS

High resolution imaging techniques, such as Atomic Force Microscopy (AFM) is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale [12]. Information is gathered by “feeling” the surface with a mechanical probe. Contact mode AFM maps the nanoscale surface by monitoring the deflection of a cantilever ending with an ultra-sharp tip probe and scanned while in contact with the surface. Noncontact mode uses an oscillating cantilever and the detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever. Scanning with an atomic-force microscopy was performed for each specimen of the flat sheet membrane mats: PVDF 0.08M; PVDF 50000; PVDF 100000, at constant temperature 20°C and the two types of images were obtained: 2D and 3D surface topography. Scans were performed for each specimen at different magnification.

3 RESULTS AND DISCUSSION

3.1 TENSILE TEST OF HOLLOW FIBER MEMBRANES

The success of any separation system involving membrane depends on the quality and suitability of the membrane incorporated in the system. When designing with any polymer it is useful to know the mechanical properties, since a membrane with greater mechanical strength can withstand larger trans-membrane pressure levels, allowing for greater operational flexibility and the use of higher pressures. A simple tensile test was applied to measure the resistance of membranes to deformation and to characterize their mechanical properties.

The tensile properties of the PES HF fibre membranes are shown in Fig. 2, where the stress vs. strain for nine test samples are compared.

There are two main deformation regions in a stress strain curve: the elastic and

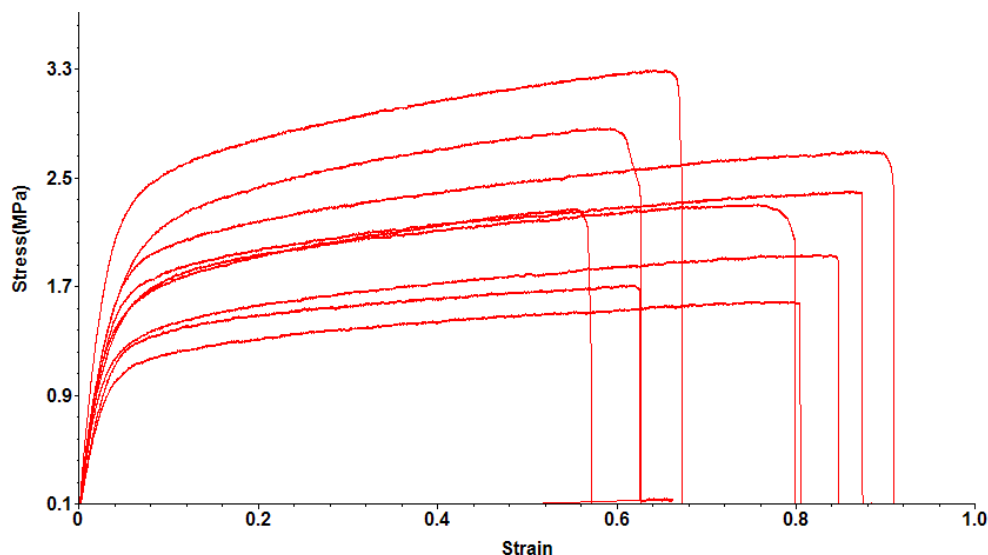


Fig. 2. (Color online) Stress (F_z) versus strain for nine fibre PES samples.

the plastic deformation. In the linear elastic region upon deformation the tensile stress increases linearly and the elementary plastic yielding is reached. After the point of yield stress (elastic limit) between 3 and 7 N, and once the yield strength is exceeded the hollow finer polymer membrane deforms plastically and the deformation becomes irreversible. Thus, the system does not revert to previous configurations upon unloading. After this point a yielding followed by a drop in stress and the force is increased slightly or remain constant on account of deformation on cross section of material. The specimen starts to yield and the specimen's cross-sectional area begins to decrease. This phenomenon occurs only in ductile materials. Significant variation in force and time at brake of the PES fibrous membranes was observed, assuming that the tensile mechanical strength strongly depends on the quality and the structural homogeneity of the tested membrane pieces. The tensile properties of nine fibrous PVDF HF samples are presented in Fig. 3 and it shows the characteristic stress-strain curve for a semi-crystalline polymer.

The PVDF curves demonstrate an initial toe region (0 to 20 N) which corresponds to the straightening of crimps in the fibrils due to the flexibility of the fibers. The breaking in separate units (waved curve in the time of destruction) shows that filaments can become separated from each other and that some filaments can take more load than others during tensile testing. The reinforced PVDF fiber membrane also shows significant deviation in force and time at rupture for the tested nine samples.

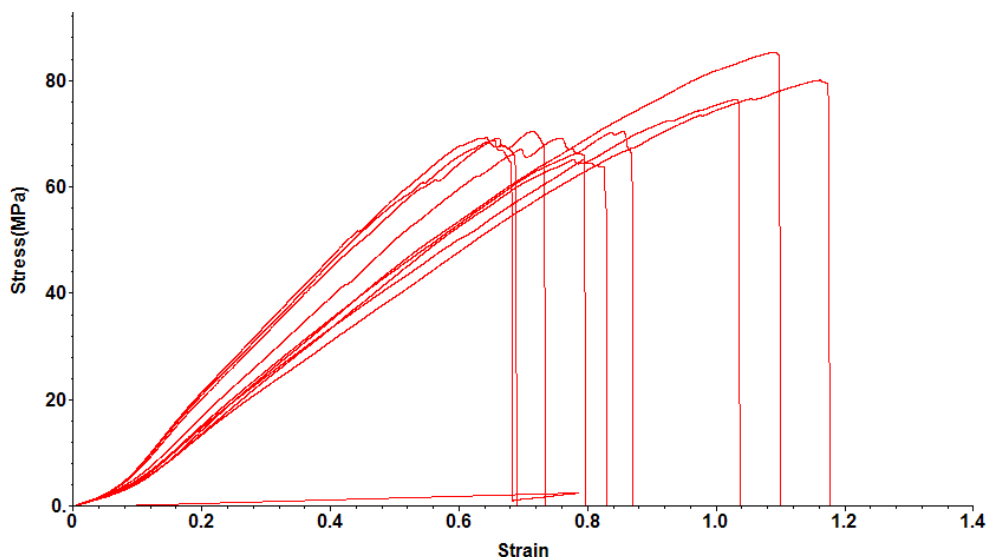


Fig. 3. (Color online) Stress (F_z) versus strain comparing nine fibre PVDF samples.

In general, the PVDF samples have more than 30 fold higher rupture force (average about 225 N) in comparison with PES samples (about 7 N). Fracture toughness may be assessed according to the size of the area below the stress-strain curve and for PVDF membranes it is many times greater. This area represents the amount of energy absorbed by the material before it fractures. The greater this area (the higher the energy required for fracture) the more ductile (or fracture resistant) the material, because more energy must be applied in order to fracture it. This difference probably due to the fact that the PVDF membrane was reinforced by a cotton fiber inserted in the inner orifice.

Mechanical properties of PES and PVDF hollow fibers membranes, as the Yield strength (MPa), Ultimate tensile strength (σ), Young's modulus (E), elongation at ultimate strength (ϵ), toughness (J/mm^3), energy at yield point (J/mm^3) are calculated and summarized in Table 2.

Yield strength is the extreme point in which the sample begins to form a "neck", or a local area which becomes gradually smaller (the cross section narrows) until a fracture is formed. Ultimate tensile strength is the maximum stress a material can withstand before failing. Young's modulus, known as the elastic modulus, is a mechanical property of linear elastic solid materials and it defines the relationship between stress (force per unit area) and strain (proportional deformation) in the material. Ultimate elongation is the total elongation just before fracture. These results

Table 2. Tensile characteristics of the PES and PVDF hollow fiber membranes

Sample	Yield strength (MPa)	Ultimate strength (MPa)	Young's modulus (MPa)	Elongation at ultimate strength (%)	Toughness (J/mm ³)	Energy at yield point (J/mm ³)
PES HF	1.45	2.06	3.76	47.66	0.49	0.04
Standard deviation	±0.211	±0.291	±1.533	±7.975	±0.109	±0.010
Standard error	±0.066	±0.092	±0.485	±2.522	±0.035	±0.003
PVDF HF	3.38	60.98	127.15	55.51	17.12	0.10
Standard deviation	±0.920	±7.786	±31.914	±12.964	±5.633	±0.050
Standard error	±0.291	±2.462	±10.092	±4.100	±1.781	±0.016

were obtained by calculating the “mean of the sum” values. The standard deviation was used to quantify the amount of variation or dispersion of a set of data values. The standard error is also presented in Table 2, as the standard deviation of the mean sampling distribution of a statistic.

Figure 4 compares all tensile characteristics of the PES (blue bars) and reinforced PVDF (red bars) hollow fiber membranes. It can be seen that both polymer mem-

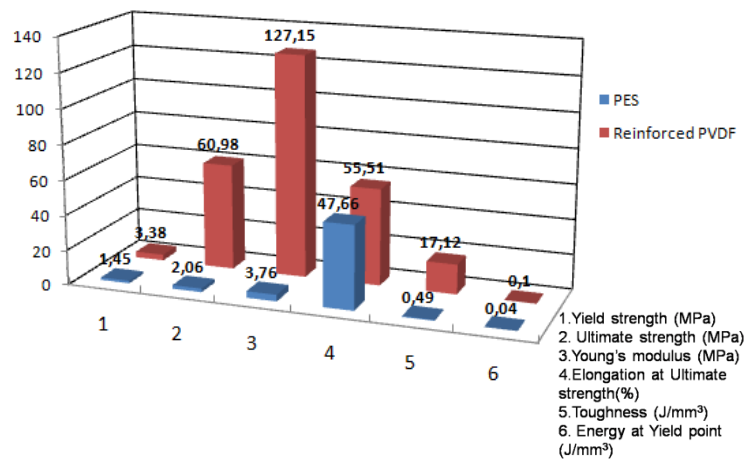


Fig. 4. (Color online) Comparison of tensile properties of PES and PVDF hollow fiber membranes.

branes, which have the same sample dimensions, demonstrate absolutely different mechanical properties. The reinforced PVDF hollow fiber membrane has around 30-fold bigger ultimate tensile strength, Young's modulus, and toughness in comparison with PES samples. Only the elongation at ultimate strength for the both types of membranes has similar values. The results show that reinforcement of the hollow fibers have a significant effect on the tensile properties. Reinforced PVDF material is stronger and tougher in big extent, but the change in elongation capability is not so pronounce compare to PES samples.

3.2 NANOINDENTATION MEASUREMENTS

Surface mechanical characteristics, such as hardness and Young modulus are determined by nanoindentation test for different type of membranes. Example load-displacement curves at maximum load of 5 mN obtained from 24 nanoindentations of the PES fibr membrane are presented in Fig. 5a. Using experimental results, Olive-Pharr model is applied for calculation of nanomechanical characteristics, such as hardness, Young's modulus of elasticity and contact stiffness [12] are presented in Fig. 5b. Hardness, H , is defined as the mean contact pressure, calculated by dividing the indenter load, P , by the projected contact area, A , at that load

$$(1) \quad H = \frac{P}{A}.$$

The projected contact area is dependent on the geometry of the indenter and it is obtained from the contact depth of the indent; h_c is calculated from the total penetra-

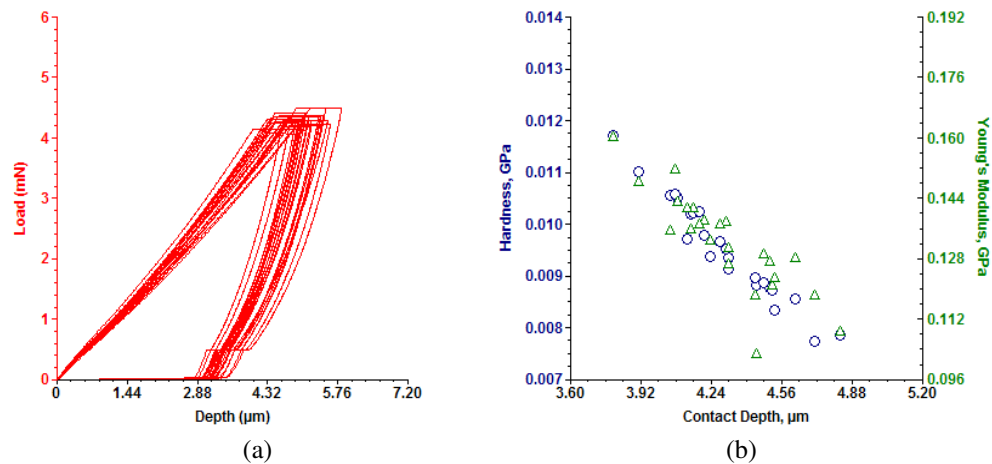


Fig. 5. (Color online) Nano-indentation results for PES fibre membrane: (a) and load-displacement curves of 24 nanoindentations; (b) calculated hardness and Young's modulus.

tion depth h , indenter load P and contact stiffness $S = dP/dh$ at the beginning of unloading. The elastic modulus for the test material, E , is then calculated using the Poisson's ratio of the test material, ν , the modulus of the indenter, E_i , the Poisson's ratio of the indenter, ν_i , and the reduced modulus E_r

$$(2) \quad \frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}.$$

For a diamond-tipped indenter, $E_i = 1141$ GPa and $\nu_i = 0.07$ GPa. The aforementioned procedure measures hardness and modulus at the maximum penetration depth of a single load–unload indent cycle.

Figure 6 (a,b) compares the load-displacement curves of two types of PVDF flat sheet membranes: (a) PVDF 0.08M, and (b) PVDF 50000 UF. As seen, the experimental load-depth curves for PVDF 0.08M membranes are shifted to higher depth values compared to PVDF 50000 UF, this indicating for lower hardness.

Table 3 summarizes the calculated values of hardness and Young's modulus for the two types PES and PVDF hollow fiber membranes, as well as the three types PVDF flat sheet membranes. Mean values of 24 indentations are presented with their standard deviation.

Results from Table 3 show that for the flat sheet membranes, the PVDF 100 000 and PVDF 50 000 UF mats demonstrate 3 times higher modulus of elasticity and hardness as compared to PVDF 0.08M mat, so they behave as a stiffer material. The very low modulus of elasticity and low hardness demonstrated by PVDF 0.08M mat shows that it is more ductile material than the others.

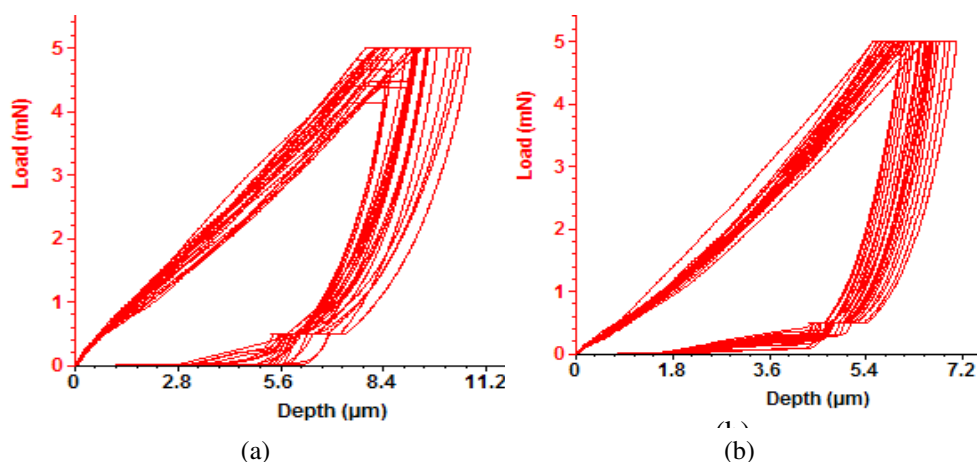


Fig. 6. (Color online) Load-displacement curves of two types flat sheet membranes: (a) PVDF 0.08M; (b) PVDF 50000 UF.

Table 3. Nanoindentation hardness and Young's modulus of all tested membranes

No	Type of membrane	Hardness, H [GPa]	Young's modulus E [GPa]
1	PES HF (hollow fiber membrane)	0.005 ± 0.001	0.043 ± 0.004
2	Reinforced PVDF HF (hollow fiber membrane)	0.010 ± 0.001	0.132 ± 0.013
3	PVDF 0.08M mat (flat sheet)	0.003 ± 0.001	0.055 ± 0.007
4	PVDF 50000 UF mat (flat sheet)	0.006 ± 0.001	0.149 ± 0.008
5	PVDF 100000 mat (flat sheet)	0.007 ± 0.001	0.151 ± 0.013

As nanoindentation results present the surface mechanical properties we could say that PVDF HF (hollow fiber membrane) show better surface performance, e.g. 3 fold higher modulus of elasticity and twice higher hardness compared to the PES HF membrane.

If compare the values of the Young's modulus of elasticity measured by instrumented indentation techniques and by the tensile measurements, it could be concluded that the values of the elastic modulus obtained from the nanoindentation tests differ from those, obtained from tensile tests. The indentation Young's modulus E shows the surface mechanical properties. The modulus of elasticity from tensile test is the overall effective modulus obtained in dynamic conditions, which demonstrates the bulk mechanical properties of the material. Differences between the effective bulk modulus and local modulus measured on a surface point are expected to exist because of local composition fluctuations and especially because the surface energy (surface tension) contribution cannot be neglected in the surface modulus. Usually, the elastic modulus of the composites measured by nanoindentation are supposed to be higher than those obtained by tensile analysis because of 1) the indentation size effect; 2) the possibility of measuring zones with higher particle density; 3) high strains relative to the elastic limit, superposed hydrostatic stress and assumptions of contact at the indent perimeter; and 4) for polymers material pile-up at the indent perimeter and non-linear viscoelasticity, etc. [8, 10, 11].

3.3 AFM MEASUREMENTS

AFM images reveal the difference in the surface topology of membrane material [13]. Figure 7 (a-c) present example AFM 2D and 3D images as comparing the three PVDF flat sheet membranes. The AFM images show different type cereal structure of: (a) PVDF 0.08M; (b) PVDF 50 000; and (c) PVDF 100 000 at the same scan size of $5 \mu\text{m} \times 5 \mu\text{m}$. The PVDF 0.08M membrane has the height distribution (z) varying from 50 to 1000 nm, but the large part of surface has roughness of 400–700 nm. This sample obviously possesses the rougher, reliever and textured surface compare to

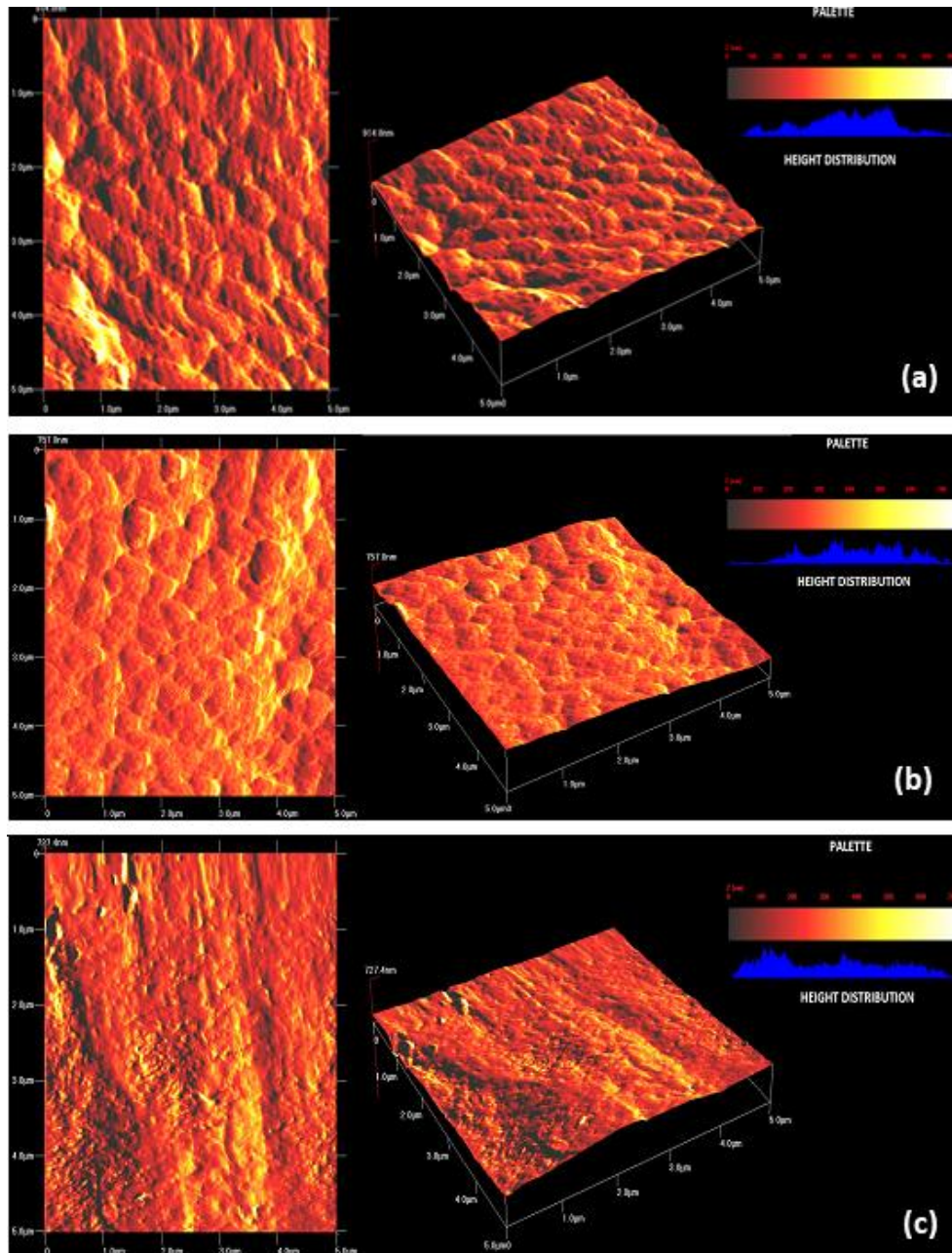


Fig. 7. (Color online) AFM images from left to right: 2D topology and 3D topology images of: (a) PVDF 0.08M; (b) PVDF 50000; and (c) PVDF 100000 flat sheet membranes at scan size $[5 \mu\text{m} \times 5 \mu\text{m}]$.

rest membranes. The PVDF 50000 and PVDF 100000 membranes have lower height distribution (z) from 0 to 700 nm. If refer to the surface mechanical properties the PVDF 0.08M membrane demonstrates the lowest hardness and modulus of elasticity compared to other two membrane mats. Obviously, the membranes with rougher surface show bigger dispersion of results and lower mechanical characteristic. The AFM measurement show that smoothest surface belongs to PVDF 1000 000 with roughness 100–200 nm and it has better hardness performance from nanoindentation test.

4 CONCLUSIONS

Mechanical properties of hollow fiber membranes and flat sheet membranes have been investigated at macro and nanoscale and related to the structure. Results for hollow fiber membranes show that the reinforced PVDF HF have 30-fold higher tensile characteristics (strength, modulus, and toughness) compared to the PES HF. Moreover, PVDF HF shows better surface performance as tested by nano-indentation, e.g. 3-fold higher modulus of elasticity and twice higher hardness if compared to the PES HF membrane.

A comparison of surface mechanical properties (hardness and Young's modulus) of three flat sheet PVDF membranes with their surface structure (roughness) demonstrates that the membranes with rougher surface (e.g PVDF 0.08M) show bigger dispersion of results and lower mechanical characteristic compared to other two membrane mats with smoother surface. The AFM measurement show that smoothest surface belongs to PVDF 1000 000 with roughness 100-200 nm and it has the best surface mechanical performance obtained from nanoindentation test.

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