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Mechanical properties of polymeric microfiltration membranes

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A R T I C L E I N F O Keywords: Microfiltration membranes Stress-strain response Tensile tests Plastic deformation Bubble point pressure	The influence of the pore topology and polymer properties on mechanical characteristics of asymmetric poly- ethersulfone (PES) and symmetric polyvinylidene fluoride (PVDF) microfiltration membranes was investigated by conducting elongation, creep, stress relaxation, small-amplitude oscillatory and bubble point pressure tests. The main aspects of the membrane stress-strain curves were found to be similar despite significant differences in the pore topology and polymer properties. While the Kelvin-Voigt model for solid polymers described the membrane viscoelastic response below the transition to ductile yielding, the stress-strain curves of membranes and solid polymers above the yield point appeared to be drastically different. All tested membranes demon- strated weak strain hardening, low sensitivity to strain rate, significant elastic recovery, stress relaxation and reduction of the bubble point pressure with accumulation of plastic deformation. Therefore, tensile stresses exerted on a membrane under assembling and process conditions should be smaller than the yield stress to assure that they will not impair filter performance. The novelty of our approach is the use of models for perforated plates to evaluate membrane mechanical properties as ductile yielding for both proceeds via localized plastic deformation around pores. Presented results provide a reliable framework for development of membranes with properties tailored to applications.

1. Introduction

Polymeric microfiltration membranes with pore sizes ranging from $0.05\,\mu m$ to $5\,\mu m$ and porosity of 70-80% are used for removal of suspended particles, drops, cells, and macromolecules from a liquid passing through a membrane in numerous industries ranging from petroleum refining to water treatment, milk and whey processing and to cold sterilization of beverages and pharmaceuticals [1]. Membranes can be arranged in filtration equipment in pleated, spiral wound or hollow fiber forms. A flat membrane sheet, typically formed by phase inversion, is subjected to large deformations caused by bending, rolling, and pleating in unit assembly and then by pressure and temperature cycles in operation. Therefore, engineering design of filtration process with membranes requires evaluation of the membrane ability to withstand deformation in the course of fabrication and operation. Prediction of the polymer stress-strain behavior is widely employed in design and manufacturing of products in the plastics industry [2,3]. However, it is rarely used in the membrane industry so that measurements of the membrane mechanical properties are usually limited to elongation and strength at break. The reason is that most experimental data and models for predicting the stress-strain behavior of solid polymers are limited to non-porous materials [4–6].

Mechanical properties of a porous polymer material depend not only on the polymer properties but also on the pore topology [7,8]. Considerable progress recently made in understanding mechanical properties of porous materials is related to cellular polymeric foams that have a high compressive strength as compression is accommodated by reducing porosity [7,8]. Most of studies in this area focus on foam compression as their primary industrial applications are related to compressive shock mitigation and energy absorption [9]. In models for a polymeric foam, a material is represented by a periodic array of interconnected solid struts and plates that form the edges and faces of cells packed together [7,8]. These models were recently adopted to evaluate the influence of deformation of a polymeric membrane at an elevated temperature (to have it sufficiently ductile) on the pore aspect ratio, pore alignment and surface roughness in order to improve the membrane filtration performance [10–17]. While these studies brought some understanding of changes in the membrane structure under deformation, models for polymer foam compression are of limited use to predict the membrane stress-strain behavior in stretching. This

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Fig. 1. EMD Millipore's membranes PES A, B, C and PVDF D. SEM images (*left to right*): cross-section, shiny and dull sides. Images of shiny and dull sides of membranes PES A, B, C have different scale bars because a substantially higher magnification needed to show a representative area of shiny sides.

deficiency motivated us to develop experimental data and models for the stress-strain behavior of polymeric microfiltration membranes under tensile loading as they are usually exposed to stretching in fabrication and operation.

Uniaxial elongation, creep, stress relaxation, and small-amplitude oscillatory tests were carried out on specially designed as well as commercially available asymmetric polyethersulfone (PES) membranes and symmetric polyvinylidene fluoride (PVDF) membranes. PES and PVDF membranes were chosen because they are widely used in separation processes due to outstanding filtering performance, high chemical and mechanical resistances and good thermal stability [18,19]. PES is a non-crystalline polymer with the glass transition temperature $T_g \sim 210-230$ °C and the melting temperature $T_m \sim 340-390$ °C. PVDF is a semi-crystalline (30–70%) polymer with $T_g \sim -41$ °C to -38 °C and $T_m \sim$ 140-180 °C. Therefore under testing conditions, the parent polymer was in the glassy state in PES membranes and with its amorphous phase in the rubbery state in PVDF membranes. All membranes were taken from the same batch and tested in as-received condition to provide a common reproducible basis for repeating tests and comparison of mechanical properties of as-received membranes from different manufacturers.

The main focus of conducted mechanical tests was on the following characteristics: elastic modulus that characterizes stiffness by defining the ratio of stress to strain at relatively small deformation, yield stress that determines the force required to initiate plastic deformation, strain hardening in the course of plastic deformation that specifies an increase in the applied force to continue deformation once initiated, sensitivity of strength to strain rate and stress relaxation at constant deformation to split the stress into a relaxed and a non-relaxed part. The impact of plastic deformation accumulated in loading-unloading cycles on the membrane bubble point pressure was investigated as it characterizes changes in the size of larger membrane pores [1]. Measurement of a bubble point pressure was conducted to characterize the effect of membrane deformation on filtration performance because it is widely used in many industries as a non-destructive test of structural changes that a filter can experience under process conditions. Constant beforeand-after filter test values reassure that there was no pore-size alteration that impaired the filtration performance.

Compared to the parent polymer, mechanical properties of a membrane are drastically weakened by the presence of pores. The observed response of membranes to tensile loading was found to be welldescribed by microscopic models developed for the weakening effect of pores on mechanical properties of perforated plates. Plates perforated with arrays of circular holes have been intensively studied for several decades due to the widespread use in heat exchangers, pressure vessels, acoustic screens, and building construction. Current methods for stress analysis of perforated plates that establish the basis for the Boiler and Pressure Vessel Codes in the U.S. and many other countries employ the concept of an equivalent solid (i.e., unperforated) plate having the same dimensions and boundary deformations as the actual perforated plate, but whose mechanical properties, called effective, account for the weakening effect of holes [20]. Presented experimental results demonstrate that the methodology developed for stress analysis of perforated plates provides a reliable framework for stress analysis of polymeric microfiltration membranes. Moreover, it is shown that microfiltration membranes meet a stringent requirement for which mechanical characteristics measured in in-plane tensile tests can be used for analysis of membrane deformation in bending that substantially simplifies measuring membrane properties.

2. Experimental

2.1. Materials

Most tests were carried out on specimens cut from rolls (width 28.1 cm) of Millipore polyethersulfone (PES) hydrophobic membranes (referred to as A, B, and C) and a roll of Durapore® polyvinylidene fluoride (PVDF) hydrophilic membrane (referred to as D). These rolls provided by EMD Millipore, Billerica, MA were fabricated by an immersion casting process with the roll centerline in-line with the rolling machine direction. Membranes PES A, B, and C are asymmetric having one "open" dull side with larger pores compared to the pores of the other "tight" shiny side (Fig. 1). By filtering from the open to the tight side, the upstream polymer matrix acts as a pre-filter, capturing larger particles and agglomerates, thereby protecting the tight region and preventing clogging. The polymer solution concentrations and casting process variables were designed to achieve different pore sizes and different degrees of asymmetry. As a result, the pore size rating in the tight region is 0.1 µm in membrane A and 0.2 µm in membranes B and C. Compared to membrane B. membranes A and C have as a sharper transition from smaller to larger pores (Fig. 1). The porosity of membranes A, B, and C is within 70-80% and their thicknesses are 110 µm, 140 µm, and 180 µm, respectively. The membrane PVDF D is symmetric with the porosity 75%, the pore size rating 0.2 µm, and the thickness 125 µm. It also has a shiny side and a dull side because the pores are cone-shaped (Fig. 1).

For comparison, a number of similar tests were also conducted on the commercially available membrane disc filters from Pall Corporation, NY: hydrophobic asymmetric Supor®-200 PES (diameter 90 mm, thickness 145 μ m, nominal pore size 0.2 μ m) and Supor®-800 PES (diameter 90 mm, thickness 140 μ m, nominal pore size 0.8 μ m), and hydrophilic symmetric FP-Vericel® PVDF 200 (diameter 47 mm, thickness 140 μ m, nominal pore size 0.2 μ m).

2.2. Tensile testing

Uniaxial tensile tests of all membranes were performed on a texture analyzer (model TA-XT2, Stable Micro Systems Ltd., Surrey, UK; Fig. 2(a)). All tests were carried out under ambient conditions (temperature 20–25 °C and relative humidity 20–50%) maintained by the building's heating, ventilation and air conditioning system. Tests for constant strain rate, creep and stress relaxation of EMD Millipore's membranes PES A, B, C and PVDF D were conducted on specimens of approximately 60 mm long and 20 mm wide, respectively parallel and perpendicular to the direction of stretch. The specimen dimensions were taken such that the instrument was able to provide accurate and precise measurements of the elongation length and load force applied, generate enough force to rupture a specimen and allow a wide variation of the elongation speed. The elongation length and load force resolutions for these specimens were about 0.005 mm and 0.01 N, respectively. in-line with the machine direction in roll manufacturing. Specimens of the same dimensions were cut from Pall's Supor®-200 PES and Supor®-800 PES disc filters. Small-amplitude oscillatory tests of EMD Millipore's membranes were conducted on specimens $60 \text{ mm} \times 20 \text{ mm}$ and $30 \text{ mm} \times 20 \text{ mm}$. Differences between data on specimens of different sizes were lying within the variation from specimen to specimen of the same size. Due to a smaller diameter, tests of Pall's FP-Vericel® PVDF 200 disc filters were conducted on $30 \text{ mm} \times 19 \text{ mm}$ specimens.

A specimen was gripped between the lower crosshead and the upper crosshead of the texture analyzer (Fig. 2(a)). The upper crosshead was controlled to move up or down. The software package Exponent (Stable Micro Systems Ltd., Surrey, UK) was used to conduct (i) strain controlled tests in which the time variation of the upper crosshead displacement L(t) was specified while the force F exerted on a specimen by the upper crosshead was measured as a function of time and (ii) load controlled *tests* in which the time variation of the force F(t) exerted on a specimen was specified while the upper crosshead displacement L was measured as a function of time. Data points were sampled and stored every 0.005s. Results of these tests were expressed in terms of the engineering stress $\sigma(MPa) = F(t)/S_0$, strain $\varepsilon(\%) = 100 \times (L(t) - L_0)/L_0$, and strain rate $\dot{\varepsilon}(\%/s) = (100/L_0) \times dL/dt$, where S_0 and L_0 were respectively the initial cross-sectional area and the initial length of a specimen gripped between the lower crosshead and the upper crosshead, S_0 and L_0 were measured before any deformation had taken place; $L(t) - L_0$ represented the specimen elongation.

2.3. Bubble point pressure measurements

An apparatus for measuring the bubble point pressure was assembled using a dead-end stainless steel membrane holder provided by EMD Millipore, a pressure gauge (IR ARO, PR4021-100, 150 psi (10.3 bar) maximum supply, Ingersoll Rand, Davidson, NC) and a pressure regulator (Model 0–100 psi (6.9 bar), CECOMP Electronics Inc., Libertyville, IL). All tests were conducted on specimens of diameter 47 mm.

The bubble point pressure was measured on hydrophobic and hydrophilic membranes. Since the use of water for measurements on hydrophobic membranes requires high pressures, experiments were carried out using isopropyl alcohol (IPA) with a low surface tension. A specimen was preconditioned by wetting with IPA and placed into the holder. IPA was then added. The upstream air pressure was gradually increased until a steady stream of bubbles was noticed to exit.

2.4. Scanning electron microscopy (SEM)

A field emission scanning electron microscope (FESEM) LEO1530VP GEMINI (Carl Zeiss, Peabody, MA, USA) was used to examine the membrane structure. Specimens for analysis were cut out of a tested membrane and coated with carbon using a sputter coater (Bal-Tec MED 020 HR).

2.5. Differential scanning calorimetry (DSC)

DSC curves of specimens of PES A membrane exposed to stress were recorded on a Mettler Toledo DSC, Columbus, OH, USA. The calorimeter was calibrated with a Mettler Toledo indium sample. Measurements were conducted on 3.0-3.9 mg specimens cut and stacked inside a $40 \,\mu\text{L}$ semi-hermetically sealed aluminum crucible. Specimens were heated from room temperature to $250 \,^{\circ}\text{C}$ at a rate of $10 \,^{\circ}\text{C/min}$.

Specimens were cut off along or across the roll centerline that was



Fig. 2. (a) Photos of a texture analyzer TA-XT2, Stable Micro Systems Ltd., Surrey, UK with a membrane specimen stretched until ruptured at a constant rate of 33.3%/s. (b) Stress-strain curves at different strain rates. EMD Millipore's membranes PES A, B, C and PVDF D, specimens cut along the roll centerline: solid lines for strain rate 1.67%/s and dash lines for 33.3%/s. Pall's FP-Vericel® PVDF 200 membrane: 1-4 for strain rates 1.67, 3, 10 and 20%/ s, respectively. (c) A schematic diagram of typical regions for stress-strain curves of an amorphous polymer in the glassy state and a semi-crystalline polymer with its amorphous phase in the rubbery state [4,5]: 1, elastic; 2, strain softening; 3, strain hardening; 4, necking that ends up with the rupture; a strain rate for the solid line is higher than that for the dashed line.

3. Results and discussion

3.1. Mechanical properties of membranes

3.1.1. Stress-strain curves

The stress-strain curves of EMD Millipore's membranes PES A, B, C and PVDF D and Pall's FP-Vericel® PVDF 200 membrane are plotted in Fig. 2(b). They were generated by stretching the specimen at a constant rate and measuring the instantaneous stress until rupture. Experiments were conducted at different strain rates up to 33.3%/s that corresponded to the maximum crosshead speed of our unit. For comparison, Fig. 2(c) shows a schematic diagram for typical strength-strain curves of an amorphous polymer in the glassy state and a semi-crystalline polymer with its amorphous phase in the rubbery state [4,5]. For them, the elastic regime of deformation is followed by an overshoot with the well-developed upper and lower yield points at relatively low strain rates. Accordingly, the applied stress for solid polymers increases steadily with elastic strain until it reaches the upper yield point required to initiate plastic deformation and then drops to the lower yield point equal to the stress required to maintain yield. The next stage of polymer deformation is the strain hardening region that ends at the ultimate tensile strength point at which time a neck forms where the local cross-sectional area becomes significantly smaller than the initial (Fig. 2(c)). The necking region ends up with the rupture. As the strain rate increases, ductility of solid polymers decreases while the modulus and the yield and tensile strengths increase (Fig. 2(c)).

As can be seen in Fig. 2(b), the stress-strain curves of membranes differ drastically from the behavior of solid polymers in Fig. 2(c). All membranes exhibited a rather sharp transition to ductile yielding and weak strain hardening in the course of plastic deformation. Rupture of tested membranes occurred without noticeable necking. An increase in the membrane strength during ductile yielding caused by a twentyfold increase in the strain rate was lying within 6–15% for all membranes Therefore, the tensile strength of a membrane at break was rather close to the stress at which yielding began (Fig. 2(b)). Tests of EMD Millipore's membranes were carried out on specimens cut along and across the roll centerline. The strength at break of these specimens was observed to vary with location along the roll centerline by up to 3–8% with the magnitude to be typically greater for specimens cut along the roll. The magnitude of the strength at break appeared to be more



Fig. 3. (a) Pall's FP-Vericel® PVDF 200 membrane. Elastic recovery following applied strains 20% and 40% for strain rates (1) 1.67%/s; (2) 20%/s. (b) EMD Millipore's membranes. Dependence of residual strain on applied strain at strain rates 1.67%/s (solid symbols) and 33.3%/s (open symbols); specimens cut along the roll centerline. (c) Photos of EMD Millipore's PVDF D membranes: (1) virgin membrane and membranes stretched at strain rate 1.67%/s for different applied strains (listed second number provides residual strain): (2) 10%, 3.1%; (3) 20%, 9.0%; (4) 30%, 15.8%; the rightmost image shows that plastic deformation accumulated by virgin membrane after 30% extension transforms circle (1) drawn on it into ellipse (4); all specimens cut along the roll centerline. (d) SEM images of virgin and stretched EMD Millipore's membranes PES A (shiny side) and PVDF D. Residual strain 23.3% for PES A and 15.8% for PVDF D; membrane specimens cut along the roll centerline indicated by the arrow and stretched in the arrow direction.

reproducible for specimens taken nearby compared to the elongation at break that was observed to vary significantly from specimen to specimen (Fig. 2(b)).

Stretching membranes up to a certain elongation and then releasing the applied force for elastic recovery was used to study the accumulation of strain caused by plastic deformation $\varepsilon_{pl}(\%)$ (Fig. 3(a)). Plots in Fig. 3(b) show the dependence of the amount of plastic deformation accumulated by EMD Millipore's membranes in a loading-unloading cycle on the applied strain.

Remarkably, the residual strain along the stretching direction was insensitive to strain rate and increased linearly with the applied strain $\varepsilon(\%)$. More significantly, data points for PES A, B, C membranes fell on the same line:

PES A,B,C:
$$\varepsilon_{pl}(\%) = 0.89\varepsilon(\%) - 3.13$$
; PVDF D: $\varepsilon_{pl}(\%)$
= 0.64 $\varepsilon(\%) - 3.47$ (1)

with $R^2 = 0.999$ for both expressions. As it follows from Eq. (1), EMD Millipore's membranes began to accumulate plastic deformation in a loading-unloading cycle at $\varepsilon > 3.53\%$ for PES A, B, C and $\varepsilon > 5.46\%$ for PVDF D. It is important that elastic deformation of a membrane equal to $\varepsilon_{el} = \varepsilon - \varepsilon_{pl}$ continued to increase in the course of ductile yielding, thereby increasing with the applied strain $\varepsilon(\%)$ as

PES A,B,C:
$$\varepsilon_{el}(\%) = 0.11\varepsilon(\%) + 3.13$$
; PVDF: $\varepsilon_{el}(\%) = 0.36\varepsilon(\%) + 3.47$
(2)

It is interesting that specimens did not acquire residual contraction in the direction transverse to loading as illustrated by photos in Fig. 3(c). As can be seen in these photos, a circle drawn on a virgin membrane appeared elliptical as the membrane was stretched due to accumulated plastic deformation. SEM images (approximately 38 μ m x 23 μ m) of the virgin and stretched EMD Millipore's membranes PES A (shiny side) and PVDF D are shown in Fig. 3(b). They illustrate stretching of pores caused by plastic deformation of membranes. The specimens for SEM analysis were cut out from tested membranes (approximately 60 mm \times 20 mm). The direction of tensile loading of a membrane is indicated by an arrow.

3.1.2. Bubble point pressure

Increasing the pores with accumulation of plastic deformation in a loading-unloading cycle reduced the membrane bubble point pressure (Fig. 4). The impact of a twentyfold increase in the strain rate on the bubble point pressure fell within variation of data points from specimen to specimen at the same strain rate in Fig. 4. The larger bubble point for PES A was consistent with the smaller pore size of this membrane.

Fig. 5 shows the stress-strain curves for EMD Millipore's PES A, B, C and PVDF D specimens that were subjected twice to loading-unloading and for specimens that accumulated a similar plastic deformation in a single cycle. Accumulation of some plastic deformation in the first loading-unloading cycle shifted the stress-strain curve in the second cycle to the right, but did not change it significantly. Also, differences between the bubble point pressures of specimens subjected to one and two cycles (listed in Fig. 5) were comparable with variation of the bubble point pressure from specimen to specimen in the case of a single loading-unloading cycle in Fig. 4.

3.1.3. Transition to ductile yielding

The stress-strain curves of membranes from EMD Millipore and Pall



Fig. 4. EMD Millipore's membranes PES A, B, C and PVDF D. Impact of residual strain accumulated in a loading-unloading cycle on the membrane bubble point pressure; strain rates 1.67%/s (solid symbols) and 33.33%/s (open symbols); symbols in the upper left panel indicate the applied strain, 0% represents a virgin membrane. Specimens cut across the roll centerline.



Fig. 5. EMD Millipore's membranes PES A, B, C and PVDF D. Stress-strain curves at strain rate 33.3%/s for specimens that were subjected twice to loading-unloading with the second cycle followed immediately the first one (solid line) and for specimens that accumulated a similar plastic deformation in a single cycle (dash line). Listed are the bubble point pressures for these specimens. Specimens cut across the roll centerline.

plotted in Fig. 2 were fitted by the power-law equation with different power-law exponents for small and large strains:

$$\sigma \approx \sigma^* (\varepsilon / \varepsilon^*)^m, \tag{3}$$

where $m = m_1$ at $\varepsilon \le \varepsilon^*$ and $m = m_2$ at $\varepsilon \ge \varepsilon^*$ and ε^* is the strain of a sharp transition to ductile yielding (Fig. 2). The limiting cases of Eq. (3) represent a linear elastic body for m = 1 and a perfectly plastic body that does not demonstrate strain hardening for m = 0. The power-law coefficients for membranes were computed by using the so-called peeling method [21] that employs a sequential log-linearization of the curve. Specifically, m_2 and K_2 were calculated by fitting the long tail of the curve $ln\sigma$ vs. $ln\varepsilon$ from the sharp transition point up to the breakup point with a straight line

 $ln\sigma = K_2 + m_2 ln\varepsilon$,

whereas m_1 and K_1 were calculated by fitting this curve to a straight line over the range of strains below the transition point. The intersection of these lines gave

$$ln\varepsilon^* = (K_1 - K_2)/(m_2 - m_1)$$
 and $ln\sigma^* = (K_1m_2 - K_2m_1)/(m_2 - m_1)$.

The parameters were then refined by successive iterations. Magnitudes of σ^* and $E^* = \sigma^*/\varepsilon^*$ characterize the apparent yield stress and the apparent elastic modulus, respectively. Parameters in Eq. (3) for specimens of EMD Millipore's membranes PES A, B, C, and PVDF D cut along and across the roll centerline are respectively listed in Table 1. In Table 2, they are listed for specimens of Pall's membranes Supor[®]-200 PES, Supor[®]-800 PES, and FP-Vericel[®] PVDF 200. As can be seen in Tables 1 and 2, Pall's membranes had substantially lower mechanical strength compared to EMD Millipore's membranes.

The transition to ductile yielding occurred at a relatively low strain $\varepsilon^* \sim 2 - 3\%$ (Fig. 2) for all membranes. Values of ε^* listed in Table 1 are lower than the threshold to accumulation of plastic deformation given by Eq. (1) for EMD Millipore's membranes. A range of low values of m_2 (0.1-0.2) indicates weak strain hardening of all membranes in the course of ductile yielding. Accordingly, the membrane strength at break was greater than the apparent yield stress σ^* by just 30–40%. Surprisingly, these aspects of the membrane stress-strain behavior appear to be similar for asymmetric and symmetric membranes having the base polymer respectively in the glassy and with its amorphous phase in the rubbery state. As can be seen in Tables 1 and 2, a twentyfold increase in the strain rate raised the apparent yield stress σ^* and strain ε^* by 5–20% and reduced E^* by 2–20%, depending on a membrane specimen. To check statistical significance of these observations, the F-test was conducted on all data points in Tables 1 and 2 that were obtained on multiple specimens of the same membrane. While the trend of increasing σ^* , ε^* and reducing E^* was also observed on average values, changes caused by an increase in the strain rate were smaller than variation of membrane characteristics from specimen to specimen measured at the same strain rate, i.e., the F-calculated value was smaller than the F-critical value for the $\alpha = 0.05$ level of significance.

Comparison of magnitudes of the apparent yield stress σ^* and the apparent elastic modulus E^* can be used to characterize the influence of the pore topology and the base polymer properties on the membrane mechanical behavior. Measurements on asymmetric PES and symmetric PVDF membranes from EMD Millipore and Pall (Tables 1 and 2) clearly demonstrate that σ^* and E^* decreased with increasing the pore size and the sharpness in the pore size asymmetry in asymmetric membranes. Comparison of these characteristics in Table 1 for membrane specimens cut from a roll along and across the centerline shows that they were somewhat lower for most specimens cut across the centerline. It is likely related to machine-specific features as the roll centerline was in-line with the rolling machine direction.

3.1.4. Creep

Creep and stress relaxation tests were carried out to study the timedependent behavior of EMD Millipore's membranes PES A, B, C and PVDF D at stress and strain levels above σ^* and ε^* (Table 1) that specified a transition to ductile yielding (Fig. 2). A creep test was performed by applying a constant force to a specimen and measuring the variation of stress, strain and strain rate with time until rupture occurred. Experiments were conducted at stress levels close to the membrane strength at break σ_b listed in Table 1. Upon loading, the membrane elongation was initially increasing at a constant rate $\dot{\varepsilon}_c$ (Fig. 6). This stage was characterized by the balance between recovery processes and strain hardening. Then the elongation rate rapidly decreased and began to oscillate irregularly that continued until the membrane failed (Fig. 6). Rupture of membranes occurred without noticeable necking. While the time to failure t_f increased drastically with a small reduction of the loading force, the strain at break ε_b remained at the same level (Fig. 6). This finding agrees well with the classical Monkman-Grant relation $\dot{\varepsilon}_c t_f \approx \varepsilon_b$ [22] that was observed for many materials. The technological significance of this relation is that once ε_b is determined from a limited number of tests it can be used to estimate the time to rupture under complex loading conditions.

Table 1

Parameters in power-law stress-strain equation Eq. (3) for EMD Millipore's membranes.

		-							
PES A			PES B			PES C			
along ^a		across ^b	along ^a		across ^b	along ^a		across ^b	
1.67	33.3	1.67	1.67	33.3	1.67	1.67	33.3	1.67	
45 ± 7	54 ± 5	54	18 ± 3	17 ± 6	27	16 ± 3	21 ± 1	27	
9.1 ± 0.4	10.7 ± 0.2	8.8	5.5 ± 0.1	6.0 ± 0.3	6.1	4.5 ± 0.2	4.9 ± 0.1	4.5	
1.02 ± 0.04	1.11 ± 0.02	0.62	0.93 ± 0.08	1.21 ± 0.09	0.93	0.78 ± 0.04	1.16 ± 0.06	0.57	
0.11 ± 0.01	0.11 ± 0.01	0.14	0.14 ± 0.01	0.14 ± 0.01	0.16	0.17 ± 0.01	0.18 ± 0.01	0.19	
2.7 ± 0.1	3.2 ± 0.1	2.2	2.7 ± 0.1	3.1 ± 0.1	2.8	2.5 ± 0.1	2.8 ± 0.1	3.0	
6.6 ± 0.2	7.7 ± 0.1	5.9	4.3 ± 0.1	4.8 ± 0.1	4.3	3.2 ± 0.1	3.4 ± 0.1	3.0	
$246~\pm~7$	$246~\pm~10$	240	158 ± 3	156 ± 4	152	130 ± 4	$123~\pm~2$	97	
		PVDF D							
		along ^a						across ^b	
		1.67			33.3			1.67	
		29 ± 4			21 ± 5			26	
		7.1 ± 0.3			7.3 ± 0.1			6.1	
		0.92 ± 0.08			1.09 ± 0.0	6		1.18	
		0.12 ± 0.01			0.11 ± 0.0	1		0.14	
		2.9 ± 0.1			3.5 ± 0.2			2.6	
		5.4 ± 0.2			6.0 ± 0.2			4.5	
		188 ± 7			170 ± 14			169	
	PES A along ³ 1.67 45 ± 7 9.1 ± 0.4 1.02 ± 0.04 0.11 ± 0.01 2.7 ± 0.1 6.6 ± 0.2 246 ± 7	PES A $along^a$ 1.67 33.3 45 ± 7 54 ± 5 9.1 ± 0.4 10.7 ± 0.2 1.02 ± 0.04 1.11 ± 0.02 0.11 ± 0.01 0.11 ± 0.01 2.7 ± 0.1 3.2 ± 0.1 6.6 ± 0.2 7.7 ± 0.1 246 ± 7 246 ± 10	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	PES A PES B along ^a across ^b along ^a 1.67 33.3 1.67 1.67 33.3 45 \pm 7 54 \pm 5 54 18 \pm 3 17 \pm 6 9.1 \pm 0.4 10.7 \pm 0.2 8.8 5.5 \pm 0.1 6.0 \pm 0.3 1.02 \pm 0.04 1.11 \pm 0.02 0.62 0.93 \pm 0.08 1.21 \pm 0.09 0.11 \pm 0.01 0.11 \pm 0.01 0.14 0.14 \pm 0.01 0.14 \pm 0.01 2.7 \pm 0.1 3.2 \pm 0.1 2.2 2.7 \pm 0.1 3.1 \pm 0.1 6.6 \pm 0.2 7.7 \pm 0.1 5.9 4.3 \pm 0.1 4.8 \pm 0.1 246 \pm 7 246 \pm 10 240 158 \pm 3 156 \pm 4 PVDF D I.67 I.67 <td colsp<="" td=""><td>PES A PES B along^a across^b along^a across^b 1.67 33.3 1.67 1.67 33.3 1.67 45 \pm 7 54 \pm 5 54 18 \pm 3 17 \pm 6 27 9.1 \pm 0.4 10.7 \pm 0.2 8.8 5.5 \pm 0.1 6.0 \pm 0.3 6.1 1.02 \pm 0.04 1.11 \pm 0.02 0.62 0.93 \pm 0.08 1.21 \pm 0.09 0.93 0.11 \pm 0.01 0.14 0.14 \pm 0.01 0.14 \pm 0.01 0.16 2.7 \pm 0.1 3.1 \pm 0.1 2.8 6.6 \pm 0.2 7.7 \pm 0.1 5.9 4.3 \pm 0.1 4.8 \pm 0.1 4.3 246 \pm 7 246 \pm 10 240 158 \pm 3 156 \pm 4 152 PVDF D along^a 1.67 33.3 33.3 29 \pm 4 21 \pm 5 7.1 \pm 0.3 7.3 \pm 0.1 0.19 \pm 0.0 0.12 \pm 0.01 0.11 \pm 0.0 0.11 \pm 0.0 0.29 \pm 0.1 3.5 \pm 0.2 5.4 \pm 0.2 6.0 \pm 0.2 1.67</td><td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td><td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td></td>	<td>PES A PES B along^a across^b along^a across^b 1.67 33.3 1.67 1.67 33.3 1.67 45 \pm 7 54 \pm 5 54 18 \pm 3 17 \pm 6 27 9.1 \pm 0.4 10.7 \pm 0.2 8.8 5.5 \pm 0.1 6.0 \pm 0.3 6.1 1.02 \pm 0.04 1.11 \pm 0.02 0.62 0.93 \pm 0.08 1.21 \pm 0.09 0.93 0.11 \pm 0.01 0.14 0.14 \pm 0.01 0.14 \pm 0.01 0.16 2.7 \pm 0.1 3.1 \pm 0.1 2.8 6.6 \pm 0.2 7.7 \pm 0.1 5.9 4.3 \pm 0.1 4.8 \pm 0.1 4.3 246 \pm 7 246 \pm 10 240 158 \pm 3 156 \pm 4 152 PVDF D along^a 1.67 33.3 33.3 29 \pm 4 21 \pm 5 7.1 \pm 0.3 7.3 \pm 0.1 0.19 \pm 0.0 0.12 \pm 0.01 0.11 \pm 0.0 0.11 \pm 0.0 0.29 \pm 0.1 3.5 \pm 0.2 5.4 \pm 0.2 6.0 \pm 0.2 1.67</td> <td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td> <td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td>	PES A PES B along ^a across ^b along ^a across ^b 1.67 33.3 1.67 1.67 33.3 1.67 45 \pm 7 54 \pm 5 54 18 \pm 3 17 \pm 6 27 9.1 \pm 0.4 10.7 \pm 0.2 8.8 5.5 \pm 0.1 6.0 \pm 0.3 6.1 1.02 \pm 0.04 1.11 \pm 0.02 0.62 0.93 \pm 0.08 1.21 \pm 0.09 0.93 0.11 \pm 0.01 0.14 0.14 \pm 0.01 0.14 \pm 0.01 0.16 2.7 \pm 0.1 3.1 \pm 0.1 2.8 6.6 \pm 0.2 7.7 \pm 0.1 5.9 4.3 \pm 0.1 4.8 \pm 0.1 4.3 246 \pm 7 246 \pm 10 240 158 \pm 3 156 \pm 4 152 PVDF D along ^a 1.67 33.3 33.3 29 \pm 4 21 \pm 5 7.1 \pm 0.3 7.3 \pm 0.1 0.19 \pm 0.0 0.12 \pm 0.01 0.11 \pm 0.0 0.11 \pm 0.0 0.29 \pm 0.1 3.5 \pm 0.2 5.4 \pm 0.2 6.0 \pm 0.2 1.67	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a Data based upon three specimens.

^b Data based upon one specimen.

Table 2

Parameters in power-law stress-strain equation Eq. (3) for Pall's membranes.

Membrane	Supor [®] -200 PES ^a		Supor [®] -800 PES ^a		FP-Vericel [®] PVDF 200 ^b	
Strain rate $\dot{\epsilon}$, %/s	1.67	33.3	1.67	33.3	1.67	20.0
Elongation at break ε_b , %	16	15	12	18	63 ± 11	53 ± 9
Strength at break σ_b , MPa	4.0	4.1	2.1	2.8	2.5 ± 0.1	2.5 ± 0.1
m_1	0.97	1.04	0.94	0.73	0.95 ± 0.04	0.98 ± 0.17
m_2	0.15	0.17	0.21	0.21	0.08 ± 0.01	$0.08~\pm~0.01$
Strain ε^* , %	2.3	3.0	2.3	2.8	1.5 ± 0.04	1.9 ± 0.09
Stress σ^* , MPa	3.0	3.2	1.5	1.9	1.9 ± 0.1	2.0 ± 0.1
Modulus E^* , MPa	130	107	65	68	127 ± 11	$105~\pm~8$

^a Data based upon one specimen.

^b Data based upon four specimens.



Fig. 6. EMD Millipore's membranes (a) PES A, (b) B, (c) C and (d) PVDF D. Creep under a constant force; strain rate averaged over 0.2 s-interval. Specimens cut along the roll centerline.



Fig. 7. EMD Millipore's membranes (a) PES A, (b) B, (c) C and (d) PVDF D. Stress relaxation under constant strain; loading strain rate 0.83%/s. Stretching was completed at the time instant t_i . Specimens cut along the roll centerline.

Table 3

Parameters in stress relaxation equation Eq. (4) for EMD Millipore's membranes.

PES A Membrane PES B PES C Direction relative to roll centerline along^a across along^a across along across 0.657 ± 0.008 0.640 0.677 ± 0.006 0.661 0.663 ± 0.007 0.656 a_{∞} 0.124 + 0.0020 1 2 1 0.111 + 0.0030.115 0.110 + 0.0030 1 1 6 a_0 0.142 ± 0.005 0.144 0.130 ± 0.007 0.130 0.120 ± 0.005 0.128 a_1 0.078 ± 0.011 0.098 ± 0.007 0.096 0.082 ± 0.009 0.093 0.100 a_2 90.8 ± 2.7 95.4 91.7 ± 2.7 92.2 91.6 ± 1.8 91.6 τ_0 , s 4.5 ± 0.1 5.0 4.6 ± 0.1 4.7 4.8 ± 0.2 τ₁, s 4.8 0.19 ± 0.03 0.22 0.20 ± 0.03 0.23 0.23 ± 0.04 0.23 τ₂, s PVDF D Membrane Direction relative to roll centerline along across 0.657 ± 0.003 0.656 a_{∞} a_0 0.137 ± 0.002 0.137 0.142 ± 0.005 0.142 a_1 0.064 ± 0.009 0.065 a_2 92.7 ± 3.5 91.0 τ_0 , s 4.7 ± 0.4 4.3 τ₁, s 0.18 ± 0.04 0.17 τ_2, s

, -

^a Data based upon four specimens.

3.1.5. Stress relaxation

A stress relaxation test was performed by stretching the specimen to a certain elongation at a constant strain rate and measuring the stress required to maintain that elongation as a function of time. This test determined a relaxed and a non-relaxed part of the stress. Experiments were carried out on membrane specimens at stress levels lower than the membrane strength at break σ_b listed in Table 1. Six specimens of each membranes were prepared, four cut along the roll centerline and two across. All specimens were stretched at a strain rate of 0.83%/s and held for 5 min sufficient to reach a steady stress value. Surprisingly, the stress relaxation curves measured at two different levels of deformation, one strain was about twice the magnitude of the other, can be superimposed by taking the ratio between the stress magnitude after a certain period of time, $t - t_l$, and the stress σ_{max} at the time instant t_l when stretching was completed. Accordingly, the curves $\sigma (t - t_l)/\sigma_{max}$ are plotted in Fig. 7.

Equation (4) that includes a constant a_{∞} for the fraction of the remaining stress and three exponential decays was found to fit well the stress relaxation curves of membranes. The resolution of our unit was insufficient to determine shorter relaxation times.

$$\frac{\sigma(t-t_l)}{\sigma_{max}} \approx a_{\infty} + a_0 exp\left(-\frac{t-t_l}{\tau_0}\right) + a_1 exp\left(-\frac{t-t_l}{\tau_1}\right) + a_2 exp\left(-\frac{t-t_l}{\tau_2}\right),$$
(4)

where the decay amplitudes a_0 , a_1 , and a_2 and relaxation times $\tau_0 > \tau_1 > \tau_2$ were computed using the peeling method [21]. Parameters a_0 and τ_0 were found by fitting the slowest tail

$$ln(\sigma(t-t_l)/\sigma_{max}-a_{\infty})$$
 vs. $(t-t_l)$

to a straight line. This term was then subtracted from the transient data set and the procedure was repeated to compute a_1 and τ_1 . Similarly, a_2 and τ_2 were computed by subtracting two terms from the transient data. Next, all parameters were refined by successive iterations.

Parameters in Eq. (4) for specimens of EMD Millipore's membranes PES A, B, C, and PVDF D cut along and across the roll centerline are listed in Table 3. Fitting the relaxation curves by Eq. (4) indicates that stress relaxation of membranes can be described by a generalized Maxwell model widely used for solid polymers [6]. In this model, a_{∞} represents contribution of an elastic element. Exponential decays in Eq. (4) represent viscoelastic elements, each formed by a viscous dashpot and an elastic spring, whose contributions to the total stress are given

^b Data based upon two specimens.

by coefficients a_0 , a_1 , a_2 [4–6]. These terms describe accumulation of plastic deformation.

Using data in Tables 1 and 3 and Fig. 7, the ratio $a_{\infty}\sigma_{max}/\sigma^*$ was found to range between 0.6 and 1.0 for all membrane specimens. It means that the contribution of the elastic element to the stress above the yield point σ^* is greater than the total contribution of viscoelastic elements in Eq. (4) representing accumulation of plastic deformation. It is interesting that a_0 and a_1 appeared to be comparable for all membranes but τ_0 was twentyfold larger than τ_1 . Drastic differences between times τ_0 , τ_1 , τ_2 in exponential decays in Eq. (4) indicate that stress relaxation was caused by the molecular processes on extremely different time scales [4-6]. Identification of molecular groups associated with these processes was beyond the capability of our unit. A certain similarity between parameters in Eq. (4) (Table 3) for asymmetric membranes and symmetric membranes with different pore topology and base polymer suggests that the stress relaxation is mainly associated with polymer molecules around pores being a common feature to all membranes.

3.1.6. Small-amplitude cyclic loading

Small-amplitude oscillatory tests

 $\varepsilon = Acos(2\pi\nu t)$

with A = 1.66% and different frequencies ν were used to study the response of EMD Millipore's membranes PES A, B, C and PVDF D and Pall's membrane FP-Vericel® PVDF 200. The maximum strain A was about 60% of the transition to ductile yielding ε^* for EMD Millipore's membranes and about 90% for FP-Vericel® PVDF 200 (Table 1). The strain rate amplitude $2\pi\nu A$ varied in these tests from about 5%/s to 70%/s. A membrane specimen was subjected to a tensile stress when the upper crosshead was moving up and partly when it was moving down. Once the membrane became compressed, it easily buckled into a curved shape. Tests at each frequency were repeated twice. Stress-strain curves for these tests are presented in Fig. 8.

The area within the hysteresis loop of a stress-strain curve in Fig. 8 represents the energy losses in a loading and unloading cycle that provides a measure of dampening in the polymer. Widening of the hysteresis loop with increasing frequency for all membranes indicates the growth of the amount of energy lost during oscillations. Analysis of Fourier components demonstrated that the measured variation of stress with time can be well fitted by three terms as the contribution of higher-frequency components was found to be statistically insignificant:

$$\sigma \approx \sigma_0 + \sigma' \cos(2\pi \nu t) - \sigma' \sin(2\pi \nu t),$$

where σ_0 represents the average compressive stress while σ' and σ'' specify the dynamic storage E' and loss E'' moduli and the phase lag δ between stress and strain:

$$E' = \sigma'/A$$
 and $E'' = \sigma''/A$ with $E = \sqrt{E'^2 + E''^2}$ and $tan\delta = E''/E'$
(5)

Parameters in Eq. (5) for specimens of EMD Millipore's membranes cut along and across the roll centerline and Pall's membrane FP-Vericel[®] PVDF 200 are listed in Table 4. Values of σ_o ranging from -0.4 MPa at low frequencies to about -0.03 MPa at high frequencies were substantially smaller than σ' for all membrane specimens. The measured variation of tensile stress ($\sigma - \sigma_0$) with time was found to be well described by the Kelvin-Voigt model widely used for solid polymers [6]. This model incorporates an elastic spring and a viscous dashpot with the stress apportioned to both elements

$$\sigma = E_{KV}\varepsilon + \eta_{KV}d\varepsilon/dt \quad , \tag{6}$$

where E_{KV} and η_{KV} represent respectively the spring elastic modulus and the viscosity of the dashpot. The Kelvin-Voigt model yields $E' = E_{KV}$ and $E'' = 2\pi v \eta_{KV}$ for the storage and loss moduli in Eq. (5). Fitting data on the growth of the loss modulus with frequency to a linear expression was used to evaluate the viscosity η_{KV} listed in Table 4; fitting was achieved with R^2 ranging from 0.95 to 0.99. The retardation time of membranes $\tau_r = \eta_{KV}/E_{KV}$ that characterizes the delayed response of a membrane to an applied stress was ranging from 6 ms to 10 ms. Direct measurement of the membrane stress-strain response at this time scale was beyond the resolution of our unit. Increasing the test frequency reduced the magnitude of *E* and *E'* by 5–14% (Table 4) while it usually increases the storage modulus of solid polymers [4]. Increasing the pore size and the sharpness in pore size variation across a membrane from PES A to PES C lowered magnitudes of both dynamic moduli (Table 4). Both moduli appeared to be somewhat lower for specimens cut across the roll centerline.

To estimate the effect of oscillations on membrane properties, three specimens of EMD Millipore's membranes PES A, B, C and PVDF D cut along the roll centerline were subjected to 100 oscillations at 1 Hz. These specimens were then stretched at the strain rate 1.67%/s until rupture. The measured stress-stress curves were quantified by computing parameters listed in Table 1. The impact of oscillations was found to fall within the variation of data points from specimen to specimen without exhibiting any trend.

It is instructive to compare magnitudes of the membrane elastic modulus determined in small-amplitude oscillatory tests and tensile tests at comparable strain rates. In this regard, we took data for *E* at 3 Hz in Table 4 (strain rate 31.3%/s) and data for E^* at 33.3%/s in Table 1 for EMD Millipore's membranes and data for E^* at 20%/s for Pall's FP-Vericel® PVDF 200 membranes in Table 2. The values of *E* appear to be greater than E^* by about 4–30% for EMD Millipore's membranes, but smaller than E^* by 14–30% for Pall's FP-Vericel® PVDF 200 membranes. It indicates a "softer" transition to ductile yielding for the former and a "stiffer" transition for the latter.

To verify that membrane deformation in conducted tests did not change molecular characteristics of the polymer, we used differential scanning calorimetry (DSC) to measure the glass transition temperature T_g of specimens of EMD Millipore's membrane PES A subjected to a stretch of 30% and 40%, a stretch of 30% followed by 300s relaxation (elongation rate 1.67%/s in all tests), creep for 25 min under 15.9 N force, and compression between two plates by 1.35 MPa pressure. The values of T_g for a virgin and deformed specimens were found to lie in the range 222.5–223.5 °C. This outcome confirmed that polymer properties were not affected.

3.2. Comparison of mechanical properties between membranes and perforated plates

The novelty of our approach is demonstration that test results of membranes reported in Sec. 3.1 appear to be well captured by microscopic models developed for the stress-strain response of metal and plastic plates perforated with periodic arrays of equal circular holes. Circular holes in a perforated plate are arranged in triangular, square, staggered square and diamond patterns. The arrangement of holes is characterized by the so-called ligament efficiency

$$\eta = (p - d) / p \tag{7}$$

equal to the ratio of the minimum ligament width (p - d) to the pitch p of the hole pattern, where p is the distance between centers of two adjacent holes and d is the hole diameter [20]; $\eta = 1$ for an isolated hole and η is a very small number for densely packed holes when $(p - d) \ll p$.

To compare our experimental data on membranes with predictions of models for perforated plates, we take the membrane nominal pore size for *d* in Eq. (7). As the minimum ligament width is equal to the minimum thickness *w* of a wall between two adjacent pores, we have w = p - d and $\eta = w / p$. Next, we express the values of d/p and η in Eq. (7) in terms of the membrane porosity φ by considering pores as hollow cylinders across the membrane and using the so-called unit-cell approximation for a random arrangement of pores [7,8] that models a



Fig. 8. EMD Millipore's membranes PES A, PES B, PES C, and PVDF D (specimens cut along the roll centerline) and Pall's FP-Vericel® PVDF 200 membrane. Stressstrain curves under small amplitude oscillatory load at different frequencies. Arrows indicate the load variation.

membrane as a cylindrical cell with a single pore in the center. This model yields

 $d/p \approx \varphi^{1/2}$ and $\eta \approx 1 - \varphi^{1/2}$ (8)

If we model a membrane as a square array or a hexagonal array of equal hollow cylinders, we respectively obtain

$$\eta = 1 - 2\varphi^{1/2}/\pi^{1/2}$$
 for $\varphi < \pi/4 = 0.78$ and

$$\eta = 1 - 12^{1/4} \varphi^{1/2} / (\pi)^{1/2}$$
 for $\varphi < \pi / \sqrt{12} = 0.91$

Contrary to Eq. (8), these models are limited to a certain porosity range. In particular, a square array model is inappropriate for the tested membranes with the porosity 70–80%. Taking 75% for the porosity of all membranes, Eq. (8) yields $\eta = 0.13$ with $p = 0.9\mu m$ and $w = 0.1\mu m$ for Pall's Supor®-800 PES membrane and $p = 0.1 - 0.2\mu m$ and $w = 0.01 - 0.03\mu m$ for other tested membranes. A hexagonal array model provides a slightly smaller value $\eta = 0.09$ for this range of porosity.

As said earlier, models for the stress-strain response of a perforated plate employ the concept of an equivalent solid plate with effective mechanical characteristics that account for the weakening effect of pores [20]. This methodology can be employed when stress variations generated by an applied force are relatively small over the pitch length. In this case, stress and strain distribution in a perforated plate is first computed for the equivalent solid plate using classical constitutive equations for elastic or viscoplastic solid materials and then used to calculate the ligament stresses and strains around pores. A localized stress is evaluated using the stress concentration factor (often referred to as stress multiplier) $\sigma_{max}/\sigma_{nom}$ that is the ratio of the maximum stress σ_{max} under the actual force to some reference stress σ_{nom} [23]. This factor is specified by coefficients $K_g = \sigma_{max}/\sigma_g$, where σ_{nom} is defined as the average stress σ_{r} at the gross-sectional area far from the holes, and $K_n = \sigma_{max}/\sigma_n$, where σ_{nom} is defined as the stress σ_n in the cross section at the hole that is formed by removing the hole from the plate gross cross section [23]. These coefficients are related as $K_g = K_n \sigma_n / \sigma_g$, where the ratio σ_n/σ_g characterizes the stress gradient. While the methodology of an equivalent solid plate is approximate, it is widely used in stressstrain analysis for engineering design of perforated structures [20]. One important result is that the effective mechanical characteristics of a perforated plate in bending approach the values for in-plane deformation as the plate becomes sufficiently thick [24-27]. The reason is that bending stress is a combination of tensile and compressive stresses whose variation across the depth decreases with increasing the relative plate thickness. This approximation is acceptable when the plate thickness H is at least twice greater than the ligament pitch p. This approximation is well valid for membranes as for them the relative thickness $H/p = \varphi^{1/2} H/d \sim 150 - 1000$.

Results of numerous experimental and computational data on the stress concentration factors K_g and K_n for various periodic arrays of holes in a plate are summarized in Ref. [23]. For elastic deformation of

Table 4

Frequency dependence of parameters in equation Eq. (5) for EMD Millipore's membranes PES A, B, C, PVDF D and Pall's FP-Vericel® PVDF 200 membrane.

Membrane ^a	Along roll centerline								
Frequency	0.5 Hz 1 Hz			3 Hz			5 Hz		
PES A									
E, MPa	273 ± 12	$273~\pm~12$		257 ± 10		244 ± 14			
E', MPa	273 ± 12	273 ± 12		253 ± 10		234 ± 9			
E'', MPa	4.6 ± 0.3	12.8 ± 0.5		41.9 ± 1.2		68.4 ± 2.2			
δ , degree	< ~2	2.7 ± 0.1		9.4 ± 0.1		16.3 ± 0.1			
η_{KV} , MPa·s	2.18 ± 0.03								
PES B									
E, MPa	190 ± 6	191 ± 6		179 ± 6		170 ± 6			
E', MPa	190 ± 6	191 ± 6		177 ± 6		163 ± 6			
E'', MPa	2.5 ± 0.4	8.3 ± 0.3		$28.2~\pm~0.8$		46.9 ± 1.7			
δ , degree	< ~2	2.5 ± 0.1		9.1 ± 0.1		$16.0~\pm~0.1$			
η_{KV} , MPa·s	1.48 ± 0.05								
PES C									
E, MPa	154 ± 6	154 ± 6		145 ± 6		138 ± 7			
E', MPa	154 ± 6	154 ± 6		143 ± 6		133 ± 6			
E'', MPa	1.5 ± 0.5	6.2 ± 0.2		22.5 ± 1.1		37.8 ± 1.9			
δ , degree	< ~2	2.3 ± 0.1		8.9 ± 0.1		$15.9~\pm~0.1$			
η_{KV} , MPa·s	1.19 ± 0.06								
PVDF D									
E, MPa	231 ± 1	236 ± 3		233 ± 3		225 ± 1			
E', MPa	231 ± 1	236 ± 3		231 ± 3		219 ± 1			
E'', MPa	5.1 ± 0.9	3.8 ± 0.7		26.9 ± 0.3		52.4 ± 0.2			
δ , degree	< ~2	< ~2		6.6 ± 0.1		13.5 ± 0.1			
η_{KV} , MPa·s	1.57 ± 0.02								
Membrane ^a	Across roll centerline								
Frequency	0.5 Hz	1 Hz		3 Hz		5 Hz			
PES A									
E, MPa	251 ± 1	252 ± 1		239 ± 2		227 ± 3			
E', MPa	251 ± 1	252 ± 1		235 ± 1		218 ± 2			
E'', MPa	4.0 ± 0.6	11.7 ± 0.2		38.9 ± 0.8		64.0 ± 1.4			
δ , degree	< ~2	2.7 ± 0.1		9.4 ± 0.1		16.4 ± 0.2			
η_{KV} , MPa·s	2.03 ± 0.04								
PES B									
E, MPa	168 ± 4	168 ± 5		157 ± 5		148 ± 6			
E', MPa	168 ± 4	168 ± 5		155 ± 5		143 ± 6			
E'', MPa	2.3 ± 0.4	7.4 ± 0.2		24.5 ± 1.3		40.7 ± 2.1			
δ , degree	< ~2	2.5 ± 0.1		9.0 ± 0.2		15.9 ± 0.2			
η _{KV} , MPa·s PES C	1.29 ± 0.07								
E, MPa	118 ± 3	118 ± 3		111 ± 3		105 ± 3			
E', MPa	118 ± 3	$\pm 118 \pm 3$		110 ± 3		101 ± 3			
$E^{\prime \prime}$, MPa	1.5 ± 0.5	5.1 ± 0.1		$17.5~\pm~0.5$		$29.0~\pm~0.9$			
δ , degree	< ~2	2.5 ± 0.1		9.0 ± 0.1		$16.0~\pm~0.1$			
η_{KV} , MPa·s	0.92 ± 0.03								
PVDF D									
E, MPa	172 ± 3	176 ± 3		173 ± 2		165 ± 2			
E', MPa	172 ± 3	176 ± 3		172 ± 2		161 ± 2			
E'', MPa	3.5 ± 0.4	1.5 ± 0.3		19.5 ± 0.4		37.8 ± 0.3			
δ , degree	< ~2	< ~2		6.4 ± 0.2		$13.2~\pm~0.2$			
η_{KV} , MPa·s	1.13 ± 0.01								
Frequency	1 Hz		3 Hz		5 Hz		7 Hz		
FP-Vericel® PVDF	200 ^b								
E, MPa	86 ± 4	4	86 ± 1		83 ± 1		77 ± 1		
E', MPa	86 ± 4	4	85 ± 1		81 ± 1		74 ± 1		
E'', MPa	2.4 ±	1.9	8.1 ± 0.2		15.6 ± 0.3		$20.6~\pm~0.5$		
δ , degree	< ~2		5.4 ± 0.1		$10.9~\pm~0.2$		$15.5~\pm~0.4$		
η_{KV} , MPa·s	0.47 ±	0.02							

^a Data based upon three specimens.

^b Data based upon one specimen.

a perforated plate with the ligament efficiency of $\eta \approx 0.13$ being similar to the tested membranes, K_g and K_n range up to 26 and up to 3, respectively, depending on the pattern geometry and the orientation of an applied force with respect to the hole pattern. Due to the strong weakening effect of holes characterized by these values, the ratio of the elastic modulus of an equivalent solid plate E_{ESP} to the elastic modulus of the base material E_M at $\eta \approx 0.13$ is very low [26–29]. In particular for thick plates $H/p \ge 2$, values of the ratio E_{ESP}/E_M for a triangular pattern are isotropic and ~ 0.1 but are anisotropic for a square pattern, being ~ 0.15 in the pitch direction and ~ 0.05 in the diagonal direction [26,27].

Computational and experimental studies of perforated plate deformation revealed that plastic deformation of the plate material begins at the edge of a hole, where tensile stresses concentrate, and the plastic region then advances to the center of a ligament [25,30-34]. This tendency toward localized plastic deformation appears to be more pronounced for low ligament efficiency $\eta \approx 0.1$ due to large magnitudes of the stress concentration factors. The outcome of microscopic theories for perforated plates at a small ligament efficiency appeared to be consistent with our experimental data on membranes for deformation under the applications of stresses smaller and greater than the apparent yield stress. Specifically, the membrane deformation for the former was found to be described by the Kelvin-Voigt model for solid polymers, Eq. (6), indicating that the polymer was mainly deformed elastically, whereas it was found to be described by Eqs. (1) and (2) for the latter indicating that the polymer around pores simultaneously accumulated plastic and elastic deformations.

Numerous computer simulations for deformation of perforated plates were conducted with elastic-plastic models for the plate material to explore the complex relation between local strains of ligaments and the total strain of the plate. This relation was found to become linear at the beginning of ductile yielding when the average ligament stress exceeded the yield strength of the plate material as in this case gross yielding occurred in the majority of ligaments [30–34]. In this case, the yield strength of an equivalent solid plate (ESP) can be estimated as $\sigma_{ESP,Y} \approx \varrho \eta \sigma_Y$, where σ_Y is the yield strength of the plate material and φ is the so-called cutout factor that depends on the ligament efficiency η , the geometry of the hole pattern [35–37]. In simplified models, the value of φ is defined as the lowest limit of loading for all in-plane stress biaxiality ratios. The parameter φ increases with increasing ligament efficiency from about 0.7 at $\eta = 0.13$ to unity at $\eta = 1$ [30–34,38,39].

We now consider whether microscopic models that are widely employed for the design of mechanical properties of perforated plates, can be used to design mechanical properties of membranes. These models predict mechanical properties based on characteristics of the parental material and the configuration of holes. Since manufacturers did not provide properties of the membrane parent polymer, we took the following data for generic polymers from a database in Ref. [40]: elastic modulus 2.6 GPa and ultimate tensile strength 87 MPa for PES; elastic modulus 1.1 GPa and ultimate tensile strength 49 MPa for PVDF. The ultimate tensile strength was used as an estimate of the polymer yield stress. Taking these characteristics as E_M and σ_Y for the base polymer and parameters $E_{ESP}/E_M = 0.13$, $\eta = 0.13$, $\varrho = 0.7$ for the weakening effect of pores, the following characteristics were calculated: $E_{ESP} \approx 340 MPa$, $\sigma_{ESP,Y} \approx 7.9 MPa$ for PES membranes and $E_{ESP} \approx 143 MPa$, $\sigma_{ESP,Y} \approx 4.5 MPa$ for PVDF membranes.

The predicted values of E_{ESP} and $\sigma_{ESP,Y}$ overestimate the measured modulus E^* and yield stress σ^* of EMD Millipore's PES A membranes (Table 1) by about 30–40% and 8–10%, respectively. With increasing the pore size and the sharpness in the pore size asymmetry in asymmetric membranes, overestimate of E^* and σ^* increases to respectively 110–120% and 70–80% for EMD Millipore's PES B membranes, to 160–190% for both characteristics of EMD Millipore's PES C and Pall's Supor®-200 PES membranes, and to 370–410% for both characteristics of Pall's Supor®-800 PES membranes (Tables 1 and 2). However, the

predicted values of E_{ESP} and $\sigma_{ESP,Y}$ underestimate the modulus E^* and yield stress σ^* of EMD Millipore's PVDF D membranes by about 15–25% (Table 1) but overestimate E^* and σ^* of Pall's FP-Vericel[®] PVDF 200 by about 15–35% and 120–145%, respectively (Table 2).

Although the presented estimates appear to be crude for some membranes, they demonstrate that the models for perforated plates capture the weakening effect of pores on the membrane mechanical properties. It is conceivable that the prediction accuracy of the membrane stress-strain response will be significantly improved if the parent polymer properties are taken instead of generic data.

4. Summary and conclusions

The influence of the pore topology and polymer properties on mechanical characteristics of asymmetric PES and symmetric PVDF microfiltration membranes was investigated by conducting elongation, creep, stress relaxation, small-amplitude oscillatory and bubble point pressure tests. The main aspects of the membrane behavior were found to be similar despite significant differences in the pore topology and polymer properties.

The viscoelastic behavior of membranes below the transition to ductile yielding was well-described by the Kelvin-Voigt model for solid polymers. However, the behavior of membranes and solid polymers in ductile yielding appeared to be drastically different. All tested membranes demonstrated an abrupt transition to ductile yielding at a relatively low strain 2-3% and weak strain hardening with the strength at break greater than the apparent yield stress by 30-40%. Membrane rupture occurred without noticeable necking and with the time to failure increasing drastically with a small reduction of the loading force while the strain at break remained at the same level. In contrast to solid polymers, a twentyfold increase in the strain rate did not significantly change the membrane strength during yielding. Membranes accumulated the residual strain during ductile vielding only in the direction of stretching. The acquired residual strain was insensitive to strain rate and increased linearly with the total strain. While membranes simultaneously accumulated plastic and elastic deformation during ductile yielding, the stress magnitude above the yield point was mainly determined by the elastic deformation. Accumulation of plastic deformation reduced the membrane bubble point pressure. Obtained by fitting experimental data, Eq. (1)- (6) summarized test results to make it easier to use these findings for evaluation of the membrane stress-strain response in applications.

The practical significance of the presented results is that tensile stresses exerted on a membrane under assembling and process conditions should be smaller than the yield stress to assure that they will not cause pore-size alteration to impair filter retentivity and reduce the bubble point pressure. Another way is to control the membrane stretch below the elongation at yield. It is important to emphasize that multiple deformation cycles under this condition as well as a twentyfold increase in the strain rate do not influence the membrane yield stress. It is therefore recommended that manufacturers report the stress and elongation at yield for membranes.

Detailed comparison of data revealed similarity in mechanical properties between membranes and perforated plates. The common feature underlying this similarity is highly localized plastic deformation around pores during ductile yielding. Equations (7) and (8) expressed parameters in models for perforated plates in terms of the membrane characteristics. The ability to predict the membrane stress-strain response using models for perforated plates will pave the way to engineer filtration process and membranes with specific mechanical properties tailored to applications by adjusting the parent polymer characteristics and the pore topology. It is therefore recommended that manufacturers report mechanical properties of the membrane parent polymer.

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