Deformation modeling of polyvinylidenedifluoride(PVDF) symmetrical microfiltration hollow-fiber (HF) membrane

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Abstract

The tensile deformation behavior of polyvinylidene difluoride (PVDF) symmetrical microfiltration hollow-fiber (HF) membranes was studied. The membranes had submicron pores with a three-dimensional open-cell structure. The surface and cross section of the porous membranes were observed by FESEM (field emission scanning electron microscope) to investigate the microstructure of the cell, namely, its size and ligament geometry. During uniaxial tensile tests, the membranes underwent elastic deformation and plastic deformation. Large deformation induced pore growth along the tensile direction, resulting in an increase in water permeability. In order to establish a mechanical model for tensile deformation, the finite element method (FEM) was employed. In this model, the Kelvin polyhedron (truncated octahedron structure) was used to mimic a three-dimensional open-cell structure. A one-unit cell based on this structure was created, and a periodical boundary condition was employed for the FEM computation. The FEM model could reproduce the overall elastoplastic deformation behavior of the porous membrane and provide useful insight into the fabrication of porous membranes and reliable operation of water purification.

Keywords: Symmetrical microfiltration hollow-fiber membranes; three-dimensional porous structure; tensile deformation; finite-element method; water permeability

1. Introduction

Membrane filtration is a promising technology in the treatment of drinking and waste water, because it removes suspended solids without the addition of any chemicals[1]. Among the various types of polymeric membranes (i.e., flat sheet, hollow fiber and tubular type), hollow-fiber (HF) membranes are often used for water purification processes because they provide a large membrane area in a limited space[2, 3]. In practical operation, the accumulation of foulant on the membrane is a major obstacle to the efficient use of membrane processes. Such accumulation is routinely mitigated by physical cleaning[4-7], which includes air scrubbing, which causes the HF membranes to mechanically vibrate, consequently leading to detachment of accumulated contaminants from the membrane surface. Strong repetitive cleaning also potentially leads to fatigue damage of the HF membrane; in practice, breakage of the HF membrane on the edge of the potting in membrane modules is common [8]. To improve the fracture properties of HF membrane, membranes with high elongation and high strength have been developed by fabrication of prototypes; however, structure optimization of such membranes is still in an early stage.

Both macroscopic and microscopic dimensions of the membrane govern the mechanical strength of the membrane, and the inherent pore structure has inferior mechanical property compared with “solid” counterparts (matrix materials)[3, 9-13]. However, there is still a lack of knowledge of the relationship between three-dimensional structures of porous matrices and their mechanical characteristics (i.e., macroscopic deformation and fracture strength of the entire fiber membrane). As a result, optimization of the physical properties of porous membranes is done by trial and error.

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3 Our previous study examined the mechanical deformation and inherent pore
4 structure of polytetrafluoroethylene (PTFE) hollow-fiber membranes used for water
5 purification [14]. Structural analysis using the finite element method (FEM) based on a
6 simple pore structure model was carried out. Insight from this study may provide new
7 guidelines for improving the physical and mechanical properties of fiber membranes.
8 However, our model consists of a very simple structure with only two dimensions; it
9 needs to be extended to three-dimensional space and structure to account more
10 accurately for the relationship between microscopic property and macroscopic
11 deformation.
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24 The present study examined the deformation behavior of a polyvinylidene difluoride
25 (PVDF) symmetrical microfiltration (HF) hollow-fiber membrane under uniaxial tensile
26 loading, experimentally and numerically. We used the HF membrane, which has a
27 symmetrical structure, fabricated by a thermally induced phase-inversion process.
28 Tensile tests with various strain rates were carried out to observe the
29 mechanical properties of the membrane (i.e., stress-strain curve), including yield stress
30 and tensile strength. Furthermore, we investigated how the pore structure changed
31 according to the applied tensile strain. Water permeability as a function of the applied
32 strain was also investigated. On the basis of experimental results, we propose a
33 three-dimensional mechanical model with a porous structure and studied its behavior by
34 using FEM. The predictive model may be useful for designing structures with a given
35 polymer and porosity. The present study shed light on the structural design of pores for
36 physical cleaning and on the reliability of water purification.
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58 2. Materials and experimental setup

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The materials used in this study were hollow-fiber (HF) membranes for purification of drinking water (UNA-620A, microza[®], Asahi Kasei Chemicals Corporation, Tokyo, Japan). These are commercially available module components for water purification [15]. The matrix was crystalline PVDF (polyvinylidene difluoride). A thermally induced phase-inversion process was used to create a pore structure for the filtering process. The membrane cross section had a symmetrical microstructure. Figures 1(a)–(d) show the configuration and microstructure of the tested material. It resembles a tube and transports water through its wall. The inlet is the outer tube surface and the outlet is the inner tube surface. During use, a number of HF membranes assemble into a bundle and form a purification module. As shown in Fig. 1(a), the outer diameter is 1.23 mm and the inner diameter is 0.67 mm. The wall thickness is approximately 0.28 mm. The outer surface (Fig. 1(b)) and cross section (Fig. 1(c)) of the membrane were observed by a field emission scanning electron microscope, FESEM (JSM-7001F, JEOL Ltd.). The microstructure had a random network and an open-cell structure. The overall porosity was estimated to be 65% on the basis of density measurements. In such measurements, the volume of the HF membrane was calculated according to the inner and outer diameters, as well as the length of the membrane. The density of intrinsic PVDF (matrix material) of 1.78 g/cm³ was used.

Figure 1(d) shows a magnified cross section in Fig. 1(c). The open-cell structure consisted of a PVDF matrix ligament. The magnified view shows that the geometry of the PVDF ligament (strut) was not straight (i.e., non-uniform). We assumed that the PVDF ligament was a cylindrical shape with constriction (i.e., hyperbolic cylinder shape). In other words, the diameter of the ligament was not constant and was presumably a hyperbolic shape with maximum and minimum diameters. The ratio

between the maximum and minimum diameters was obtained from FESEM observations. Figures 2(a) and (b) show the distributions of pore size and diameter ratio, respectively*. The size of pores in Fig. 2(a), which are assumed to be spherical, indicates that the average diameter was 160 nm. In Fig. 2(b), the average ratio of ligament diameter was 0.75. This microstructure was observed uniformly through the thickness of the membrane.

Uniaxial tensile tests were performed by using a ball-screw-type universal testing machine (AG-1, Shimadzu Corp.). The HF membrane was wound around the testing fixture so that it applied uniform tensile stress to the membrane. The clamp distance corresponded to the gauge length of about 174 mm. The tests were conducted under displacement control at room temperature at strain rates of 4.8×10^{-4} , 4.8×10^{-3} , and 1.4×10^{-2} 1/s. For each test, average data of at least three measurements[†] were obtained.

3. Experimental results

3.1 Tensile-deformation behavior

Figure 3 shows the nominal stress–strain curve for each test at different strain rates. The nominal stress increased linearly with the increase in tensile strain and reached a flexion point. The stress value then increased gradually after the flexion point. Finally, it reached the final fracture point (indicated by $x^{\ddagger}$ in this figure). The fracture always occurred near the boundary of the clamped area of the fixture because

* For this measurement, we selected various areas (whose total is larger than $100 \mu\text{m}^2$). This is much larger than one pore size (about $0.02 \mu\text{m}^2$). Thus, our measurement provides the average value for entire material.

[†]We totally used 20 specimens in this study. These are in the same production lot. For FESEM observations, about five specimens were used. The remaining 15 specimens were used for the tensile tests.

[‡]Just before complete fracture, the stress drastically went down to zero. However, this decreasing curve is not indicated in the figure, since we do not discuss the fracture point.

of stress concentration. This means that the stress applied was not uniform. To address this problem, a preliminary test was conducted to determine how the HF membrane locally deformed under tensile loading. The outer surface of the membrane was marked with paint at 15 mm intervals along the longitudinal direction. During tensile loading, mark distance was measured by using a video camera to deduce the longitudinal strain distribution. We found that the tensile strain at each section had uniform distribution up to the point just before final fracture. When it reached the final fracture point, the local area where the HF membrane was wound on the fixture started necking locally, resulting in membrane fracture. This observation indicates that the testing method could apply uniform tensile stress to the membrane fiber up to just before the final fracture.

As shown in Fig.3, the stress-strain curves depended slightly on the strain rate $\dot{\epsilon}$, gradually increasing after the flexion point. Such trend is often observed in solid polymer materials [16, 17]. However, the effect of strain rate in this case may be minor. In contrast, the fracture strain was relatively scattered and thus might not be dependent on $\dot{\epsilon}$, because it depended primarily on the clamped condition and on stress concentration.

We then investigated how the HF membrane elastically and plastically deformed. In this study, loading and unloading tests were carried out as shown in Fig.4. At a predetermined tensile load, the loading was stopped and reduced to zero[§]. Several tests with various suspended loads were conducted. In all tests, the strain rate was set at 4.8×10^{-3} 1/s. Representative data are plotted in Fig.4. The chosen suspended loads were (A)

[§]After the loading was reduced to zero, the specimen was unfixed from the jig. In particular, the bottom of the membrane specimen was unclamped from the jig such that the specimen matched the completely unloaded condition (no-loading condition). As described later, this test measured the strain in a noncontact manner using a video camera.

($\sigma_n=3.53$ MPa, $\varepsilon_n=0.038$), (B) ($\sigma_n=4.75$ MPa, $\varepsilon_n=0.43$), and (C) ($\sigma_n=5.29$ MPa, $\varepsilon_n=0.72$) as shown in Fig.4.

As shown in Fig.4, the unloading curve for test (A) matches the loading curve, indicating that the specimen deformed elastically. However, in the tests (B) and (C), loading and unloading histories are not identical, and the strain remains after full unloading. We presumed that beyond the flexion point, the specimen underwent plastic deformation. After complete unloading, we carefully observed the changes in total strain. The results plotted in Fig.5(a) show the strain history after complete unloading (i.e., the specimen was left in a no-loading state for up to 72 hours (2 days)). In both tests, the strain decreased with the testing time and then reached a constant value. This is time-dependent behavior similar to viscoelastic recovery. However, the strain did not recover completely. The remaining strain values, i.e., the remaining plastic strain after complete recovery (plotted in Fig.5(b)) indicate that the plastic strain depended on the applied tensile strain. This means that the specimens from tests (B) and (C) underwent plastic deformation, with plastic strain remaining. Therefore, the flexion point in the stress-strain curve (in Fig.4) is the yield point. Thus, we can conclude that the specimen first deformed elastically and then developed a flexion point due to macroscopic plastic deformation. Such unique behavior might be due to the inherent pore structure and the properties of the PVDF matrix.

3.2 Changes in porous structure

We further investigated how the pore structure changed according to the applied tensile strain. Several tensile tests were carried out at various suspended strains, as shown in Fig.6(a). Those tests are designated as tests (1), (2), (3), (4), (5), and (6) in

Fig.6(a). After full unloading, we observed the porous structure of the surface by using FESEM (micrographs are shown in Fig.6(b)). Test (1) involved a no-loading specimen (i.e., an as-received specimen); the tensile direction follows the longitudinal direction of the graph. As shown in test (2), the range of elastic deformation indicates no changes in porous structure, as compared with that in test (1). However, test (4) produced a slightly different structure beyond the yield point, suggesting that the pore grew slightly. After further application of tensile strain, the porous structure significantly changed. We found that the pore grew along the longitudinal direction of uniaxial tension. The surrounding matrix (PVDF ligament) stretched because of plastic deformation. Therefore, the applied strain led to the thinning of the PVDF ligament. This is the mechanism of macroscopic plastic deformation of the HF membrane.

Figure 7 shows the change in pore structure with respect to the applied tensile strain. We carefully measured the pore area in each test (Figs.6(b), test (1)-(6)) and plotted the pore diameter (we assumed that the pores were spherical)**. Designations (1)-(6) for “Test code number” are the same as those in Figs. 6. After the yield stress (from test (3)), the pore size increased. This increase is due to plastic stretching of the matrix fiber. Notably, these observations were obtained after full unloading using FESEM. Therefore, our observations on pore structure may differ from those under tensile loading, i.e., the pore size (in Fig.7) was slightly smaller because of elastic recovery due to unloading.

Water permeability tests were carried out on the deformed specimens to investigate how tensile deformation affects water purification. The present HF membrane with 100 mm length was prepared. One membrane was immersed in pure water, and then pure

**This measurement procedure is the same with Figs.2.

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3 water was pulled from the inner diameter of the membrane under controlled flow
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5 velocity. Water was thus filtered through the thickness of membrane. One end of the
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7 membrane was filled with resin bond and the other was left open for pulling pure water
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9 for the water permeability test. In other words, the outer surface of the membrane was
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11 the inlet and the inner surface was the outlet. We continuously measured the
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13 pressure variation of flowing water under constant flow velocity, and then we
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15 calculated the coefficient of water permeability. Figure 8 shows the changes in
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17 coefficient of water permeability with applied tensile strain. Designations (1)–(6) for
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19 “Test code number” are the same as those in Fig. 7. The water permeability significantly
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21 increased when plastic deformation was large. This increase occurred because of the
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23 increase in pore size due to the tensile loading, as shown in Fig. 7. This suggests that
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25 plastic deformation of the HF membrane is critical to water purification.
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32 The results reveal that the pore structure was changed by plastic deformation of
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34 the PVDF ligament. This mechanism was a key factor in the macroscopic deformation
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36 and water purification functionality of the hollow-fiber membranes. To establish the
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38 computational approach for simulating the macroscopic deformation of the membrane,
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40 we then employed FEM incorporating the pore structure.
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46 **4. Mechanical model**

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48 A computational approach was established to predict the tensile deformation
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50 behavior of the present PVDF hollow-fiber membranes. As discussed above, the
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52 macroscopic deformation depends on the elastoplastic properties of PVDF matrix and on
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54 the inherent porous structure. Thus, a three-dimensional (3D) FEM model including the
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56 pore structure was constructed (Section 4.1). We then explored the agreement between
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the computed and experimental stress–strain curves. In this process, both elastic and elastoplastic analyses were conducted to investigate whether the computational and experimental stress–strain curves agree (Section 4.2).

4.1 Finite element simulation

Figures 9(a)–(d) present a model of the porous structure for the FEM computation. The SEM image of the open-cell structure is shown in Fig. 9(a) (see Fig. 1(d)). To model the three-dimensional porous structure, a Kelvin polyhedron type was used in Fig. 9(b). A truncated octahedron structure was chosen to enable space filling of an open cell [18, 19]. Figure 9(c) shows a collective model using the Kelvin polyhedron, which was schematically drawn by using three-dimensional CAD software (Inventor, Autodesk Inc.). As shown in Figs. 1 and 2, a porosity of 65% and an average pore diameter of 160 nm were used to create the Kelvin polyhedron structure. As shown in Fig. 9(d), we extracted one unit cell from the collective structure and applied a periodic boundary condition for the FEM computation. We noted that the matrix ligament surrounding the pore was not straight and uniform, as shown in Fig. 2(b). As a result, the ligament (strut) of this model was not uniform, as depicted in the magnified image in Fig. 9(d). The ratio of maximum to minimum diameter determined from the SEM observations is 0.75 (Fig. 2(b)). On the basis of information obtained through observation, we created a non-uniform strut model with a Kelvin structure as shown in Fig. 9(d).

Finite element method (FEM) is carried out using Marc Mentat 2013.1.0 (MSC Software Corporation). A tetrahedral element (primary element type^{††}; Fig. 9(d)) was used. Fine meshes were created around the regions of stress/strain concentration, and a

^{††}We also used tetrahedral element with secondary element type to avoid volumetric locking. This computation result agrees with our model with a primary element type.

mesh convergence study was carried out. The numbers of nodes and elements were 72,803 and 371,090, respectively. The computed FEM model is shown in Fig.10. For this model, the left end of the unit was fixed, and the right end was extended by using a uniaxial tensile load. In addition, a periodic boundary condition was applied to the model (i.e., the side surface of the x-y plane for the z direction, and that of the x-z plane for the y direction). At the right end, the longitudinal displacement and reaction force were computed to obtain the nominal stress-strain curve, which was then compared with the experimental stress-strain curve.

Elastic and plastic deformation regions were observed (Figs.3 and 4). Thus, we conducted elastic and elastoplastic FEM analyses, respectively. For the constitutive equation, elastic deformation obeys Hook's law, and plastic deformation is non-linear equation as described in Eq.(1) (see later). The yield criterion is assumed to be Mises criterion. We employed the elastoplastic properties of the PVDF matrix obtained from the previous study [20], in which the uniaxial tensile stress and strain curve of bulk PVDF was measured. According to the study [20], the crystalline phase of PVDF was an α phase, which is the same as our specimen (as measured by Fourier transform infrared spectroscopy). The stress-strain curve during plastic deformation was approximated from the phenomenological constitutive law [14, 17]:

$$\sigma = \sigma_Y + K \varepsilon_p^n \quad (1)$$

where σ_Y is yield stress, K is the work hardening coefficient, n is the work hardening exponent, and ε_p is plastic strain. These material constants were extracted for the elastoplastic property, as shown in Table 1. Here, the yield stress was assumed to be the

offset stress at a strain of 2% (i.e., the offset yield stress, $\sigma_{2\%}$)^{††}. Although the polymer material generally showed a strain rate effect during both elastic and plastic deformation, the result shows little effect on the stress–strain curve in Fig.3. Thus, this study did not consider the strain rate effect on the elastoplastic property.

4.2 Deformation behavior

Figure 11 shows stress–strain curves obtained through both experiment (same as in Fig.3) and computations. Results of elastic analysis are indicated by an open circle ($\bigcirc$) and those of the elastoplastic analysis are represented by a triangle ($\triangle$). There is good agreement between the elastoplastic deformation observed by experiment and that derived from computations. The inserted figure shows a contour map of equivalent stress (σ_{eq}) distribution for the specimen that deformed plastically. It reveals that the PVDF ligament (strut) stretched plastically, resulting in pore growth. Pore size was also investigated by FEM. As an example case, the pore diameter was $0.2\ \mu\text{m}$ when the tensile strain was 0.43, which is in good agreement with the experimental result ($0.28\ \mu\text{m}$). This agreement suggests that our computation may also be useful for predicting microscopic properties such as pore size.

The results for Young's modulus (E) and σ_Y (proof stress, $\sigma_{2\%}$) are presented in Table 2. Although these material constants are dependent on ε (see Fig.3), the computational curve reasonably agrees with that from the experiments. Thus, our model is useful for simulating tensile deformation behavior.

^{††}The offset yield stress (proof stress) is usually set to $\sigma_{0.2}$ at 0.2% strain, but the polymer material sometimes undergoes nonlinear elastic deformation. Thus, several studies use the offset stress at 2% ($\sigma_{2\%}$) (see the study by Rae et al.[15]).

To summarize, we established a 3D computational model for predicting the nonlinear deformation behavior of PVDF symmetrical microfiltration hollow-fiber (HF) membrane. The model incorporates representative pore structure and matrix properties, and it can estimate macroscopic tensile deformation. Our computational framework may be useful for various materials with pore structure and may provide insight into material fabrication and operation (e.g., optimization of a physical cleaning process with minimal mechanical deformation, new fabrication method to improve the mechanical property, and prediction of membrane operation lifetime, from the viewpoint of long-time use and recycling efficiency).

5. Conclusion

This study proposed a computational framework to simulate the tensile deformation behavior of PVDF symmetrical microfiltration hollow-fiber membranes. The HF membranes had submicron pores with a three-dimensional open-cell structure. We first observed the microstructure surface and cross section of the membranes by FESEM to investigate their pore structure (i.e., cell size and geometry of the ligament/strut). Their porosity was found to be 65%. Uniaxial tensile tests revealed that the HF membranes underwent elastic deformation and plastic deformation. Large tensile deformation induced PVDF ligament stretching and pore growth, resulting in increased water permeability. This result suggests that the water filtration capacity decreased.

FEM was employed to establish a mechanical model for tensile deformation. In this model, a Kelvin polyhedron (truncated octahedron structure) was used to mimic a three-dimensional open-cell structure. A one-unit cell based on this structure was created,

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3 and a periodic boundary condition was employed for the FEM computation. Our FEM
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5 approach successfully predicted the overall elastoplastic deformation of the HF
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7 membrane. It will yield a new guideline for optimizing the relationship between the
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9 porous structure and mechanical performance (rigidity, yield, and tensile strength) in the
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11 near future. Since the present model takes into account the pore structure, this insight
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13 may be useful for fabrication of porous membranes and for reliable operation of water
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15 purification.
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Fig.3 Experimental nominal stress–strain curves at various strain rates.

Fig.4 Nominal stress–strain curves of repeated loading–unloading tests.

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Fig.11 Nominal stress–strain curvesfrom experiment and FEM(circle: elastic analysis, triangle: elastoplastic analysis). Experimental data were obtained from Figure 3.

Table 1 Mechanical properties of the PVDF solid matrix.

Table 2 Mechanical properties (Young’s modulus and yield stress)obtainedfrom the experimental stress–strainand FEM computationalcurves(see Fig.11).

Fig. 1 Configuration and microstructure of the hollow-fiber membrane; (a) macroscopic view of cross section, (b) outer surface, (c) cross section, and (d) magnified view of (c).

(a)

(b)

Fig. 2 Distribution of pore size (a) and diameter ratio of ligament (b) of the hollow-fiber membrane.

Fig. 3 Experimental nominal stress–strain curves at various strain rates.

	○(A)	□(B)	◇(C)
σ_n , MPa	3.53	4.75	5.29
ε_n	0.038	0.43	0.72

Fig. 4 Nominal stress–strain curves of repeated loading–unloading tests.

	○(A)	□(B)	◇(C)
σ_n , MPa	3.53	4.75	5.29
ε_n	0.038	0.43	0.72

(a)

(b)

Fig. 5 Changes in total strain as a function of testing time after full unloading (a), and plastic strain with respect to the applied strain (b).

Test	(1)	(2)	(3)	(4)	(5)	(6)
σ_n , MPa	0	3.53	4.71	5.29	6.46	6.94
ϵ_n	0	0.04	0.43	0.72	1.49	1.70

(a)

(b)

Fig. 6 Nominal stress–strain curve (a) and micrographs from several tensile tests at various suspended strains(b).

Fig. 7 Changes in pore size with respect to the applied strain. The designations of (1)-(6) are the same with the legend of Fig.6(a).

Fig. 8 Changes in coefficient of water permeability with the applied strain. The designations of (1)-(6) are the same with the legend of Fig.6(a).

Fig. 9 FEM model of the 3D open-cell structure and SEM image of the porous structure with an open cell in a hollow-fiber membrane (a), Kelvin cell structure (b), cluster of Kelvin cell foams (c), and one unit cell extracted from the cluster model from panel (c) (d).

Fig. 10 FEM model of one unit cell in Fig.9(d) under the boundary condition.

Fig. 11 Nominal stress–strain curves from experiment and FEM(circle: elastic analysis, triangle: elastoplastic analysis). Experimental data were obtained from Figure 3.

Table 1 Mechanical properties of the PVDF solid matrix.

Young's modulus E , MPa	Poisson's ratio ν	Yield stress σ_Y , MPa	Work hardening strength K , MPa	Work hardening exponent n
928	0.4	26.0	30.0	0.6

Table 2 Mechanical properties (Young's modulus and yield stress) obtained from the experimental stress-strain and FEM computational curves (see Fig.11).

	Young's modulus E , MPa	Yield stress σ_Y , MPa
Exp. ($\dot{\epsilon} = 4.8 \times 10^{-3}$)	124	4.1
Exp. ($\dot{\epsilon} = 4.8 \times 10^{-4}$)	113	3.7
FEM	84	3.3