Synchrotron X-ray nanotomography and three-dimensional nanoscale imaging analysis of pore structure-function in nanoporous polymeric membranes

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ABSTRACT

3D nanoporous structures of a set of bicontinuous microemulsion-fabricated polymeric membrane films were examined using synchrotron X-ray nanotomography imaging. The interconnected pores across the membrane were displayed as visualized traces by a track analysis, where the ratio of the total length of the trace divided by the membrane thickness represented the tortuosity of the porous structure and indicated a correlation with reduced oxygen transmissibility through the membranes. 3D volume renderings of the membrane provided pore morphology with interconnected channels and quantitative porosity. The results indicate the potential use of this nanoscale imaging technique in assessing the structure-related transport properties of nanostructured functional materials.

1. Introduction

The development of functional materials with nanometer-scale structures is essential for applications involving molecular transport, including drug delivery, molecular and chemical sensing, therapeutic contact lenses, and membrane separation processes. Fabrication methods for the many materials currently used in these applications, such as bicontinuous microemulsion polymerization (BjEP), provide inherently poor control over the morphological properties of the materials, including their tortuosity, pore size distribution, and pore channel connectivity.

Scanning electron microscopy (SEM) continues to be the primary imaging tool used to analyze porous surface morphologies in various porous-structured materials. An important limitation of SEM observation is that the specimens must be conductive because nonconductive specimens tend to become charged when scanned by the electron beam, which causes scanning faults and other image artifacts. Therefore, nonconductive polymeric specimens are usually coated with an ultrathin layer of an electrically conductive material to reduce the effect of overcharge. Unfortunately, the coating can obscure the fine features of the sample at very high magnification. Other techniques, such as atomic force microscopy (AFM) or dynamic laser speckle autocorrelation spectroscopy, are also restricted to probing mainly the surface morphology in nanoporous thin films.

Transmission electron microscopy (TEM) can provide three-dimensional (3D) nanoscale morphology information of various specimen types, including biological structures and nanoporous polymeric systems, via electron tomography. However, only very thin specimens (typically less than 1 µm) can be used to take a series of 2D projections at different angles by tilting the specimen with respect to the electron beam in the TEM column, after which a 3D image of the specimen is produced via computerized tomography at a nanoscale resolution.

Micro X-ray computed tomography (microCT), which has been widely used in biology, is another promising technique to provide both 2D and 3D images of porous materials. The contrast in the images is determined by the mass absorption coefficient of the components in the sample. With rotation of the sample, 3D images are obtained, which can be used to determine the porosity, pore size, and pore interconnectivity of the sample. In contrast to physisorption and porosimetry, microCT can assess both connected and isolated pores. However, the relatively low resolution of microCT (micrometer scale) has limited its further development and application. With the rapid advancement of materials science, improvements in the resolution of this imaging technique are urgently needed. Specific internal pore architectures are...
required to provide the needed functions, such as molecular transport or biological cell infiltration, and in-growth performance for nanostructured materials. However, the key challenge of evaluating 3D pore structures in materials intended for functional applications has not been sufficiently investigated because of the absence of convenient high-resolution 3D imaging methods. In this study, we report a new three-dimensional nanotomographic imaging study of a BµEP-fabricated nanoporous polymeric film using monochromatic synchrotron X-ray and zone-plate optics, enabling Zernike phase contrast and quantitative analysis of pore structures with interconnecting channels.

2. Materials and methods

2.1. Materials and sample preparation

Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and ethylene glycol dimethacrylate (EGDMA; Merck) were purified under reduced pressure before use. The redox initiator consisted of a mixture of N,N,N′,N′-tetramethylethylenediamine (TMEDA; > 99% purity; Aldrich) and ammonium persulfate (APS; > 98% purity; Aldrich), which were used as received. SDS (> 99% purity; Sigma) was used as received. Hexadecyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) of purity greater than 98% were recrystallized from an acetone–ethanol mixture (3:1, v/v) before use. Water was purified through a Milli-Q water system to achieve a conductivity of ca. 1 μs cm⁻¹.

Glycidyl methacrylate (GMA, MW = 142.15) and 3-[tris(trimethylsilyl)propyl] methacrylate (MW= 422.81) were purchased from Sigma-Aldrich (USA). The polymerizable surfactant PEO-R-MA-40 was synthesized as described previously [15].

A silicon surfactant, Silmer ACR A008-UP (MW = 632), was purchased from Siltech Co. (Canada).

2.2. Bicontinuous microemulsion polymerization

The compositions of the bicontinuous microemulsions were used to prepare various nanoporous membranes (summarized in Table 1). Three membranes were prepared by thermal polymerization, and one membrane was prepared by the UV crosslinking of the silicon monomer. HEMA was used as the aqueous component of each microemulsion sample to obtain comparable amounts of non-aqueous and aqueous fractions, which are required to form a bicontinuous microemulsion. A crosslinking agent, EGDMA, was added to each sample to a proportion of 4.0 wt% based on the total weight of hydrophobic monomer or HEMA. A reactive redox initiator consisting of a mixture of TMEDA and ammonium persulfate (APS) was used for polymerization. The amount of APS used was 0.3 wt% based on the total weight of hydrophobic monomer or HEMA. The non-aqueous phase (HEMA 36 wt%/GMA 13 wt%/EGDMA 1.0 wt%/PEO-R-MA-40 20 wt%) was vortexed, followed by treatment with ultrasound. Water (30 wt%) and AIPH (2,2-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 0.3 wt%) were added to the mixture of the non-aqueous phase, and treated with ultrasound while on an ice bath. Mixtures were poured into the glass plates separated by aluminum foils, and further BµEP processing was continued for 1 h at 60 °C in an oven.

In M4 membrane polymerization, the aqueous phase (water 43.60% and HEMA 13.62%) was vortexed for 20 s and then mixed for 10 s after a photoinitiator, 2-hydroxy-2-methylpropionophenone (0.41%), was added to the mixture. The non-aqueous phases (EGDMA, 0.41% and silyloxyl methacrylate monomer, 12.26%) were added sequentially to the mixture and then mixed for 10 s and 20 s, respectively. Finally, the polymerizable surfactant Silmer A008-UP (29.70%) was added, and the resulting mixture was mixed for 20 s prior to being poured into the glass plates. UV polymerization was carried out for 15 min with a UV polymerizer (250–450 nm).

2.3. Synchrotron X-ray nanotomography

To investigate the interconnected pore structures of the membranes fabricated through BµEP, three-dimensional (3D) CT imaging was performed at the 7C beamline in the Pohang Accelerator Laboratory using a monochromatic X-ray beam with an energy of 6.78 keV and zone plate optics, as described previously [16]. The experimental layout of the CT imaging setup is depicted in Fig. 1. Typically, the field of view was 50 μm with a resolution of 40 nm. The detector comprises a thin (18 μm) LS0:TB scintillator crystal (FEE, Germany) with a 10-μm diameter and a 20× homemade optical microscope. The microscope was composed of a 20× objective lens (Zeiss) and a charge-coupled device (CCD, Apogee Imaging Systems; model U16M). The CCD has 4096 × 4096 pixels, each 9 μm in size. For Zernike phase contrast, a holed aluminum-film phase plate of 3.78 mm ± < 0.04 mm thickness (Luxel, USA) was positioned near the back focal plane of the zone plate. The thickness was chosen to phase shift the diffracted beam by π/2, making the sample image darker in the bright field. A membrane sample with a size of 50 × 80 μm² in a capillary was mounted onto a goniometer to acquire 360 projection images by rotating in 0.5° increments through 180° with an exposure time of 0.5 s/projection. 3D volume images of the specimen were obtained by applying a filtered back-projection algorithm to the projection image using the Octopus software package (Ghent University, Belgium). The reconstruction into volume segments and rendering were performed with the Amira software (VSG Inc., Burlington, MA).

2.4. Pore channel analysis by volume rendering

The selected volume segmentation and rendering were performed using the Amira software, and the volume of each pore was measured, enabling the porosity [porosity = (Vpore/Vtotal) × 100] of each BµEP membrane to be calculated. Within the selected segment volume, the connectivity among each pore was analyzed with 3D volume rendering of the examined pores, and the channel is noted in the figure. The average number of connectivities was estimated by counting the entire number of pore channels and dividing by the total number of pores within a segment. Final average number of pore interconnection was obtained from averaging the values of five different segments selected in each membrane.

2.5. Pore channel track analysis

Nanopores were identified on the basis of the intensity of an imaging slice falling below a preset threshold. After a nanopore was selected in the first imaging slice through the thickness direction, the nearest connected nanopore in the next slice was investigated and determined by the following algorithm. When a nanohole was selected
in the n-th imaging slice, the connected nanohole in the (n+1)-th slice was determined by finding the nearest-pore from the projected point on the (n+1)-th slice and the channel between the two on the basis of matching the pre-set intensity. The unit thickness of each 36-nm slice was used to evaluate the pore channels in each membrane. The algorithm for the track analysis of pore channels was prepared according to the procedure below.

1. The center position (Cx, Cy)n of a selected nanopore in the n-th slice was determined.
2. The center of circle Cn was then projected into the (n+1)-th slice. Typically, twelve to fifteen nanopores were identified within the specified circle Cn+1 while increasing the diameter of the circle by 20 nm from an initial diameter of 100 nm.
3. The center position of each nanopore identified in the (n+1)-th slice was newly calculated.
4. The nanopore with the smallest distance from (Cx, Cy)n to the centers of the pores in the (n+1)-th slice was chosen as the nearest nanopore in the (n+1)-th slice.
5. The interconnecting channel between Cn and a chosen nearest pore was identified by assessing the pre-set imaging intensity of the pore that was continued in the space of two consecutive, adjacent slices by starting from the center of the pore in the n-th slice and moving to the center of the pore in the (n+1)-th slice. The procedure 4–5 were iterated with the next-nearest pore until the condition was met for identified nearest pores.

The nearest connecting pores were traced as a line, and the line’s total length (TL) was measured from the top surface of the membrane to the bottom. The TL was divided by the membrane thickness (TT), giving a ratio (TL/TT) as an effective scale of tortuosity, which may be relevant to molecular transport through the membrane. Oxygen transmissibility or tortuosity was obtained from averaging over either three measurements or three different regions with initially-selected pores in each selected membrane, respectively.

To estimate the correlation of tortuosity with molecular transport,
oxygen permeability was measured using the polarographic method. The thickness of each polymeric membrane was measured using an electronic thickness gauge (ET-3, Rehder Development, USA). The membranes were soaked with a standard saline solution (ISO 18369-3:2006, 4.7) at 20 °C for 24 h prior to the oxygen permeability measurement, which was conducted using an O2 permeometer (201T, Createch, USA) according to ISO 18369-4:2006.

3. Results and discussion

3.1. X-ray nanotomography and segmentation analysis in comparison with other studies

Absorption contrast is not strong enough to see the internal structure in materials like organic polymers because they normally contain only the light elements that absorb less X-ray with X-ray energy dependent drop-off (~1/E^3). For such materials, one may use X-ray phase contrast method instead that showed slow drop-off in phase contrast due to energy dependence of 1/E. Although air inside porous structure in polymeric membrane provided absorption contrast to surrounding polymeric material, either conventional absorption-based microtomography or in-line phase contrast X-ray tomographic imaging [17,18] had been operated only in microscale spatial resolution, thus not resolving nanoscale pore structure (~100 nm). Synchrotron-based X-ray nanotomography (XNT) that employ condenser-objective provides spatial resolution of less than 100 nm and Zernike phase contrast. XNT and 3D rendering may enable the delineation of internal pore structure including connecting channels by absorptive air-filled pore, and more likely by phase contrasting polymeric materials including edge enhancement contrast from diffraction-based interference fringe. Zernike phase contrast XNT is available with either synchrotron X-ray or rotating anode X-ray source [19]. Previously, this method had been applied to analyze either polymeric (pore size; 200–800 nm) [20] or solid (pore size; 300–1000 nm) [21,22] nanoporous membrane. Both XNT studies worked on nanostructured composite (containing inorganics) with relatively larger pore size compared with our sample (50–150 nm), smallest nanopore investigated by XNT to our best knowledge), and employed just 2D projection image [20] or different way of calculating tortuosity based on Laplace diffusion equation [21].

Segmentation was chosen as a processing in sub-images from typical imaging processing tools in consideration of computational time. Skeletonization also a mathematical algorithm that processes the data locally (in sub-images) while preserving global properties [23]. They are commonly used in image analysis and pattern recognition, as they can synthetically describe shapes and mathematical properties of objects, for example length or surface area. Homotopic skeletonization algorithm may provide whole network among similar shaped objects [24], whereas track analysis in this work allows to find distance-based connectivity through channel between pores with shortest path in layer-by-layer, where pore and channels were determined by image intensity not by shape.

3.2. 3D volume rendering of pore structures

The porous polymer materials were clearly viewed with tomographic imaging, where relatively hypo-intense pores were imaged by X-ray absorption by air in the tomographic cross-section, allowing 2D images of the nanoporous BmEP films to be generated, as shown in Fig. 2A. Although apparent visibility of pore in the surface feature of SEM images as shown in Fig. 2 is not reflecting the limitation of SEM in analyzing nanoporous membrane, it is not enough to assess porous structure such as porosity, distribution, pore connectivity with channel. Those porous features were easily recognized by its volume rendering in XNT imaging, with quantitative assessment of volume and shape. A typical pore of M2 was elongated along the applied direction of the electric field and was similar in average size with smaller standard deviation than the pores of M1 (see Fig. 3 and Table 1), suggesting relatively less inhomogeneity in pore size distribution by an alignment effect from electric field in their polymerizing aggregation. M3 and M4 were produced with methacrylate derivative, which possesses relatively bulky hydrophobic groups, and polymerizable surfactants as the non-aqueous component; this process resulted in more extensive aggregation of the polymeric materials and smaller pore sizes (one-third) than were observed in M1 and M2, which were composed of simple methacrylate and an ionic non-polymerizable surfactant.

Local porosity was estimated by calculating the subtotal volume of pores in a given segment of the membrane, as summarized in Table 1. Porosity was then estimated as the ratio of the total volume of the selected pores within a given segment to the whole volume of the segment. Average porosity and average individual pore volume were obtained from analysis of five selected segments from whole reconstructed volume of each membrane (Table 1). Standard deviation represented the heterogeneity of porous structure in each membrane. Conventional methods for the measurement of porosity—physiosorption and porosimetry—give average characteristics for overall porous polymers [11], in contrast to the typical porosity of several partial volume segments obtained using this imaging-based porosity measurement technique. The adsorption method is suitable for characterizing materials that contain micropores and mesopores [25,26]. The porosimetry technique is based on the capillary law, which governs the penetration of liquid into small pores. The selection of both the theoretical model (e.g., identification of pore shape) and the experimental conditions strongly affects the measured values of porosity and pore size [27,28]. In contrast, imaging-based measurement of porosity would be directed without potential discrepancy depending on experimental conditions.

3D volume rendering provided total pore volumes with a well-depicted morphology of each pore in the chosen volume of the nanoporous membrane, resulting in a directly relative ratio of pore volume to the total volume, taken as the porosity. Porosity can be modulated through various manufacturing parameters, including the composition blend and the polymerization method. All four membranes exhibited similar porosity values of around 50%, which is characteristic of nanoporous membranes formed by bicontinuous microemulsion polymerization in which hydrophobic and hydrophilic materials are bonded with surfactant and stabilized with water in an interwoven distribution. No isolated pores were identified in this interwoven structure for any of the four BmEP-fabricated membranes. A selected segment of the membrane, based on this imaging technique, is depicted in Fig. 3, which reveals the direct visualization of the interconnectivity of the pore channels as well as multiple connecting channels among nearby pores. The average number of channels per pore was estimated as 3–3.5, demonstrating the quantitative nature of interconnectivity among pores using this method. A relatively slanted pore volume was visualized with angled interconnecting channels in a typical M3 film compared to the upright channels in the silicon-based M4 BmEP film, which resulted in a more slanted trace of the interconnecting pores in the track analysis of the M4 film, as demonstrated in Fig. 4. Such morphologic features can influence molecular transport or drug-release kinetics in functional nanostructured material applications.

Interconnected pore channels facilitate molecular transport through their network; however, the presence of too many channels per pore may hinder unidirectional molecular transport, e.g., decreasing oxygen transmissibility due to the effective lengthening molecular diffusion, thus retarding molecular transport. By contrast, this property would render enhancement of the drug retention in a drug-eluting contact lens application. The slimmer-M4 membrane retaining the lowest pore connectivity exhibited larger oxygen transmissivity compared with the GMA-M3 film, despite its relatively higher tortuosity. However, more channels would be better for filtering applications by increasing the removal function due to enhanced path length and molecular permeation. In the case of a proton exchange membrane, the proton conductivity and pore structure would be strongly influenced by the
introduction of a zwitterionic surfactant, where replacement by PEO-MA-40 would greatly deteriorate its proton conductivity property [29,30]. The volume-rendered view may explain the influence of surfactant on proton conductivity by demonstrating the structural arrangement of pore connectivity. The elongated pore volume, which can potentially be induced in a zwitterionic surfactant by applying a static electric field, may facilitate molecular transport in a drug-releasing contact lens or proton exchange cell compared to a non-aligned membrane.

3.3. Track analysis of tortuosity in network pores

A pore selected in the surface image of a porous membrane was used to find the connected pores across the film thickness using a nearest-intensity-matching algorithm applied to successively reformatted ZX-imaging planes, generating a trace of pore interconnectivity through the porous membrane, as summarized in Fig. 4. Because the inter-distance-based nearest pore in the immediate slice below does not guarantee interconnection necessarily, the selection of a sufficient multiple number of nearby pores was required to establish the interconnected pore when using the imaging-intensity-based search algorithm to identify the interconnecting channel. Therefore, the resultant trace of the interconnected pores represents the smallest length across the connected channels from the pores at the top to the pores at the bottom of the membrane. Tortuosity was defined as the ratio of the total length of the measured trace divided by the film thickness, giving values of 3.24 for the electric-field-aligned CTAB-M2-membrane and 4.32 for DTAB-M1. A larger tortuosity increases the effective diffusion distance of molecules for a given thickness, hindering the efficiency of molecular transport. The observation of a higher oxygen permeability (Dk) and transmissibility (Dk/t) in the electric-field-aligned M2 membrane compared to those in the M1 membrane was consistent with the membrane’s shorter tortuosity, as shown in Table 1. In addition, the tortuosity (3.85) in the transverse plane of M2 membrane was relatively larger compared to the tortuosity (3.24) along electric-field directed one. The tortuosity in transverse directions had same scale as those of Z-direction in other membranes. These results suggest that electric field alignment of the interconnected pores may lead to the elongation of pores in the direction of thickness, resulting in shorter tortuosity and facilitating faster molecular transport through the interconnected pore channel. M3 and M4 exhibited tortuosity values of 2.30 and 2.16, respectively, and resulted in a similar degree of oxygen permeability and oxygen transmissibility.

In geometric terms, tortuosity (τ) displayed as “trace” means by the fraction of the shortest pathway through porous structure Δl and the Euclidean distance between the starting and end point of that pathway Δx, τ = Δl/Δx, physically may be most probable path representing averaged molecular transport. Yet this pathway might not be the predominant diffusion pathway of gases and does not account for constrictive pores. Membrane permeation depends on diffusion but the nature of the diffusion process depends on many factors including the phase of the system, the pore size, the size of the permeating molecules and the driving force. Therefore, flux-based tortuosity depending on the transport mode rather account for the path of least resistance. Hence,
resulting values differ appreciably. These discrepancies are reflected by the vast number of different tortuosity calculation approaches [31].

4. Conclusion and outlook

Synchrotron X-ray nanotomography imaging with spatial resolution of 40 nm was performed non-destructively on a set of bicontinuous microemulsion polymerization-fabricated membranes, with analysis of nanoporous structures. Features of porosity, 3D morphology, pore channel, pore interconnectivity, and tortuosity through the thickness were estimated using 3D volume rendering and track analysis. The results indicate the potential ability of this nanoscale imaging technique to assess the structure-mass transport properties for developing new nanostructured functional, device such as solid oxide fuel cell (SOFC), battery, drug-eluting contact lens, ultrafiltration membrane.

A 3D representation of porous structure (size, distribution, connectivity) can be used to calculate true structural parameters and carry out a detailed study of the gas transport within a porous solid oxide fuel cell (SOFC) electrode at the pore scale [21,32]. Nanoporous membranes could be directly used for drug delivery system (DDS) or they could be placed in an implant device for sustained release [33,34]. Fine tuning of composition in the hydrogel mixture with proper microstructure is critical to ensure the balance of oxygen, ion, water in bicontinuous nanostructure-based silicon contact lens that facilitates rapid exchange of oxygen through the silicone rich phase and ions through the hydrophilic phase [35]. Since solute solubility governs retention in organic solvent nanofiltration [36], comprehensive understanding of 3D nanoporous structure is necessary to evaluate the transport properties with swelling behavior. Drug loading with retention and release rate are critically dependent on 3D porous structure including tortuosity. Simple calculation and visualization of tortuosity in addition to 3D porous structure are convenient tool to assess oxygen/drug transport in drug eluting contact lens [33] or on-demand drug release in magnetically triggered membranes implantable DDS [37]. These devices exhibit increased drug/oxygen delivery rates with smaller tortuosity or with magnetically increased membrane porosity.

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References


