**3D High Spatial Resolution Visualisation and Quantification of Interconnectivity in
Polymer Films**

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Abstract

A porous network acts as transport paths for drugs through films for controlled drug release. The interconnectivity of the network strongly influences the transport properties. It is therefore important to quantify the interconnectivity and correlate it to transport properties for control and design of new films. This work presents a novel method for 3D visualisation and analysis of interconnectivity. High spatial resolution 3D data on porous polymer films for controlled drug release has been acquired using a focused ion beam (FIB) combined with a scanning electron microscope (SEM). The data analysis method enables visualisation of pore paths starting at a chosen inlet pore, dividing them into groups by length, enabling a more detailed quantification and visualisation. The method also enables identification of the central features of the porous network by quantification of channels where pore paths coincide. The method was applied to FIB-SEM data of three leached ethyl cellulose (EC)/hydroxypropyl cellulose (HPC) films with different weight percentages. The results from the analysis were consistent with the experimentally measured release properties of the films. The interconnectivity and porosity increase with increasing amount of HPC. The bottleneck effect was strong in the leached film with lowest porosity.

Keywords: interconnectivity, visualisation, 3D, porosity, polymer, focused ion beam, scanning electron microscopy, geodesic paths, geodesic channels, bottlenecks

1. Introduction

Recently, there has been growing interest in visualisation and quantification of porous networks. In order to understand how or if pores are connected within a porous network, it is of great importance (Markl et al., 2018) to be able to do this in 3D. Porous networks are found in a wide range of different materials and have major effects on the materials properties. For example, the porosity in paper contributes to the absorption properties (Axelsson and Svensson, 2010). Another example where the porous network is very important is in catalysts where the pores are impregnated with catalyst precursors (Naomi et al., 2012; Dullien, 1992). A final example is the porous network within films used for controlled drug release that acts as the transport path for the drug (Sakellariou and Rowe, 1995). The drug release can be tailored by controlling the structure of the porous network. It is therefore important to analyse and understand the characteristics of the network (Siepmann et al., 2007).

There are many different ways to quantify 3D porous networks. For example, helium pycnometry and mercury porosimetry use a gas or liquid to fill the porous network to assess the pore volume in the sample (Ferrero et al., 2002; Westermarcka et al., 1999). However, these techniques cannot capture closed pores neither can they capture the tortuosity of the pore network. One approach that allows for a more detailed analysis of the porous network is to image the material in 3D using sequential imaging (tomography) in order to study the microstructure. Some examples of these 3D techniques are confocal laser scanning microscopy (Gebäck et al., 2015), x-ray tomography (Eric and Withers, 2014) and neutron tomography (Vontobel et al., 2006). However, the spatial resolution of these three techniques is limited to the resolution of a few hundreds of nanometres (Zschech, et al., 2018). Transmission electron microscopy tomography using focused ion beam (FIB) removal of material layers, combined with scanning electron microscope (SEM) imaging are examples of techniques with higher spatial resolution (Michael, 2011; Holzer et al., 2004; Goldstein et al., 2003; Cantoni, 2014). The FIB-SEM tomography is a destructive technique where the ion beam is used to remove material in a very accurate way. This is the technique which is used in the present paper.

Quantitative pore parameters that have been used for describing porous networks are for example pore volume, pore size distribution, pore morphology, interconnectivity and tortuosity. Previous research has shown that interconnectivity strongly influences transport properties (Armatas, 2006; Vogel, 1997; Ghassemzadeh 2004; Yang et al., 2014). Geodesic paths have been used in robotics, visual computing and image analysis of gray-scale images (LaValle, 2006; Kallmann and Kapadia, 2016; Cohen and Kimmel, 1997; Soille, 2004) to describe interconnectivity, and geodesic paths have been visualized in the context of material science in

Lindquist et al. (1996) and Peyrega et al. (2013). Pore volume, pore size and pore morphology can be estimated from 2D data, but in order to extract interconnectivity, 3D data are crucial. The methods used in this paper are based on geodesic paths, which here are shortest pore paths through the porous network which lay entirely inside the pore structure. The relative length of a geodesic path compared to the length of the porous network is termed the geodesic tortuosity. The geodesic tortuosity has previously been used to predict diffusive transport with good results (Stenzel et al., 2016, Barman et al., 2018). The higher the tortuosity, the lower the diffusive transport is in general. Other types of tortuosities, such as the hydraulic, electrical and diffusive tortuosity, can be computed from fluid or diffusion measurements or simulations (Ghanbarian et al., 2013; Julbe and Ramsay, 1996; Veroort and Cattle, 2003; Vogel, 1997). An advantage with geodesic paths and geodesic tortuosity is that they are computed directly from the porous network, meaning that computationally expensive diffusive simulations, for example, are not necessary to get an idea of how tortuous paths through the porous network are.

In this work a new data analysis method for investigating the interconnectivity of 3D data based on geodesic paths is presented. Specifically, the method quantifies how the porous network is connected to a chosen inlet pore. The geodesic paths are used to visualise the structure of individual paths in 3D and to visually distinguishing trends in the structure of the paths. This is done by grouping paths by their tortuosity and visualising several paths in one image. Here the choice of a specific inlet pore is important, since it makes the images of geodesic paths less cluttered and therefore easier to interpret. As a complement to the visualisations, the geodesic paths are also used to quantify geodesic channels where many paths coincide. The geodesic channel measure is a new measure which uses geodesic paths to extract the central features of the porous network, showing the “backbone” of the porous network (Barman et al., 2020). This paper thus presents a novel method to quantitatively describe a 3D porous network with high spatial resolution. These quantitative parameters can be used to identify crucial structural features such as limiting layers with bottlenecks in the porous network. The method is applied to free-standing phase-separated polymer films. The films are used as a model system for controlled-release films on oral dosage forms. The films consists of ethyl cellulose (EC), water insoluble, and hydroxypropyl cellulose (HPC), water soluble, mixed with ethanol as solvent (Marucci, et a., 2013). A phase-separation occurs when the ethanol evaporates (Frohoff-Hülsmann, et al 1999). The two polymers form a bi-continuous network where the HPC can be removed by leaching the films in body fluids. Provided that the HPC phase forms a continuous network the resulting porous film provides transport paths for the drug. The polymer blend ratio governs the final porosity of the film and strongly influences the morphology, including the

interconnectivity of the phases. Hence, different weight percentages of HPC result in different types of pore structures (Andersson, et al., 2013). The results indicated the presence of limiting layer at the lowest percentage of HPC, marked by decreased interconnectivity and increased tortuosity with a bottleneck effect. This is consisted with the structural observations of the films. As bottlenecks are thought to be an important factor slowing down transport (Berg, 2012; Holzer et al., 2013; Siepmann et al., 2012, Ch. 9), this should have a big impact on the transport through this type of film.

2. Materials and Methods

2.1 Preparation of Porous Polymer Films for Controlled Drug Release

The porous polymer films were produced in two steps. First, an ethanol solution of ethyl cellulose (EC) and hydroxypropyl cellulose (HPC) was sprayed on a hot rotating drum described by Marucci et al. 2009. The total polymer content in the solution was 6 wt% and three films with different ratio of EC:HPC were produced ((EC: Ethocel™ Standard Premium 10 cps from Dow Wolff Cellulosic GmbH in Germany, HPC: Klucel® LF pharma grade from Ashland in USA). The dried films contained 22 wt%, 30 wt% and 45 wt% of HPC, denoted as HPC22, HPC30 and HPC45. These are respectively denoted as HPC22, HPC30 and HPC45. The overall thickness for HPC22, HPC30 and HPC45 was 133 μm , 159 μm and 150 μm , respectively. In the second step the films were put in deionised water for 24 hours, allowing HPC to leach out. After leaching, the dried porous films were mounted onto an aluminium stub with double-adhesive carbon tape, followed by deposition of a thin (a few nanometres) palladium layer onto the surface to reduce the charging effects during the subsequent imaging in the FIB-SEM. The EMITECH K550X Palladium Sputter was used with film current 25 mA, film time 3 minutes and with rotation of the specimen holder.

2.2. Focused Ion Beam Scanning Electron Microscopy Tomography

A Tescan GAIA3 (Tescan, Czech Republic) FIB-SEM was used to acquire high spatial resolution 3D. A thorough investigation was performed in order to ensure acquisition of representative 3D data of the microstructure in the material. Therefore, several subvolumes were acquired from each HPC concentration. The film surface is oriented in the plane normal to the ion beam and tilted 55° with respect to the electron beam. The ion beam was used to mill thin slices and the electron beam to image each new cross-section surface. This set-up allowed the sequential slice and image procedure to proceed without changing the orientation of the film.

The ion beam and electron beam parameters were optimised to reduce milling and imaging artefacts such as curtaining and charging effects. The ion beam parameters used for milling were 30 keV and 1 nA. The electron beam parameters used for imaging were 700 eV and 1 pA. The 2D image stacks were obtained by using the ion beam for serial sectioning with slice thickness 50 nm for 10 μm depth (z). The width of the cross-section was 45 μm and the height 35 μm . A backscattered electron detector was used, the scan speed was 2 $\mu\text{s}/\text{pixel}$ and the 10 nm pixel size. The protocol of how to optimise the FIB-SEM parameters for porous and poorly conductive materials are described in more detail in Fager et al., 2020. A few micrometres platinum layer was deposited on the film surface to further prevent from curtaining (Mayer et al., 2007). In order to reduce charging, a carbon gas precursor, (naphtalene) was injected prior to imaging with the electron beam in order to charge neutralize the cross section surface. A U-shaped trench was established to eliminate shadowing effects upon imaging of the cross-section surface (Holzer et al., 2004).

2.3 Image Segmentation

The image data were segmented into pore and solid phases using a machine learning approach, because standard thresholding methods were found to be insufficient. Briefly, manual segmentation was performed in 100 randomly selected 2-D regions of size 256x256 pixels for each data set. A set of Gaussian smoothing filters were applied to extract information at different scales (so-called linear scale-space features), using Gaussian filters with standard deviations $\sigma = 1, 2, 4, 8, 16, 32, 64$, and 128 pixels, for the slice to be segmented and five adjacent slices in each direction. For each data set, 75 randomly selected regions were used for training and the remaining 25 for testing. A random forest classification method, that combines the output of 101 decision tree classifiers, was trained and tested using the manually segmented data. The training accuracies were 97.6 %, 98.0 %, and 98.4 %, for the HPC22, HPC30, and HPC40 data set, respectively, while the test accuracies were 92.2 %, 92.4 %, and 87.0 %. After training on the manually segmented subset of the data, the algorithm was applied to the full data sets. The code was developed in-house using Matlab (Mathworks, Natick, MA, US).

2.4 Visualisation and Quantification of Interconnectivity

In order to visualise interconnectivity and to quantify channels in the porous network, geodesic paths were computed. A geodesic path, denoted $\text{GeoPath}(p)$, is defined in this context as the shortest path that satisfies the following three constraints: (1) it starts at a chosen inlet-pore, (2)

it ends anywhere at the outlet surface and (3) it passes through the point p . Choosing different points p thus gives different shortest geodesic paths. This is illustrated in Figure 1 where a 2D porous network is shown with three different points p and their corresponding geodesic paths. The geodesic paths were in this work, in contrast to the standard definition (Lindquist et al., 1996; Peyrega, C. and Jeulin, D., 2013), chosen to start at a specific inlet-pore as illustrated in the figure. This choice makes it easier to interpret images of several geodesic paths and to distinguish trends in path structure.

The geodesic tortuosity, $\tau(p) = \frac{l(\text{GeoPath}(p))}{L}$, gives the relative length of the geodesic path ($l(\text{GeoPath}(p))$ is the length of the geodesic path), compared to the height of the porous network, L . The tortuosity thus measures how much longer the geodesic path is compared to the distance between the inlet and the outlet. This means that the lowest possible tortuosity is $\tau(p)=1$. The computation of tortuosities and geodesic paths was implemented using Matlab's function *bwdistgeodesic* (Matlab, 2018).

Geodesic channels, parts of the porous network where many paths coincide, are quantified using a new method described in detail in Barman et al. (2020). This measure allows for the extraction of important features of the porous network by showing the most important connections in the network. The geodesic channel measure is computed from a large number of $\text{GeoPath}(p)$, where the points p are evenly distributed throughout the porous network. The channel measure in a voxel, termed the channel strength, gives the percentage of all computed $\text{GeoPath}(p)$ that pass through that voxel. This is computed for all voxels in the porous network. Figure 2 shows an example of the geodesic channel measure computed in the 2D porous network from Figure 1. The channel measure in the Figure 2 can be interpreted as showing the “backbone” of the porous network connecting the inlet to the outlet. The main channels, i.e. the channels of high strength, are the most important paths connecting the 2D porous network with the chosen inlet and outlet.

For the EC/HPC data, the geodesic paths were used to visualise individual transport paths and to extract the degree of interconnectivity by capturing path variations as well as quantify channels. In contrast to the 2D examples shown in Figure 1 and 2, the quantification methods were applied in 3D to the EC/HPC data. The geodesic paths were all computed in the transport direction in the films, i.e. in the y -direction shown in Figure 5. Visualisation of the individual transport paths and the extraction of the degree of interconnectivity was done by dividing the paths into categories by their tortuosity, i.e. by their relative length. First the tortuosity $\tau(p)$ of geodesic paths corresponding to all points p in the pore space was computed. Short,

intermediate and long categories were defined. The short category contained all paths that had the 20% shortest lengths, the intermediate category all paths between the 40% and 60% lengths and the long category all paths between the 80% and higher lengths. Individual transport paths were visualised for the shortest, longest and an intermediate path category. For an illustration of the degree of the interconnectivity, 40 paths were chosen randomly from each category and visualised. The paths were chosen uniformly, meaning that all paths in a category had the same probability of being chosen. We consider 40 paths to be enough to give a fair representation of the distribution of path lengths within each category. The geodesic channel measure was computed based on 10 000 GeoPath(p) for each film, corresponding to 10 000 points p that were distributed evenly throughout the porous network. That is, the geodesic channel strength in each voxel gives the percentage of the 10 000 computed geodesic paths that passed through the voxel.

3. Results and Discussion

3.1 FIB-SEM Data

Figure 3 shows 2D SEM images of cross section surfaces for each film. From Figure 3 it can be seen that the pores are not spherical. 3D reconstructions of the porous network for each film are seen in Figure 4 (rendering made using Object Research Systems, 2018). The quantification methods were applied to the 3D reconstructions.

The total pore volume and median pore size for the three films were calculated to 20 % and 0.35 μm for HPC22, 30 % and 0.60 μm for HPC30 and finally 44 % and 0.72 μm for HPC45. The pore volume and pore size were computed using Matlab (Matlab, 2018), the pore size using the morphological operation *imopen*. In this work the pore size with respect to a sphere was used. A detailed analysis with respect to anisotropy using other types of pore sizes can be found elsewhere (Barman et al., 2020). The spherical pore size distribution of the three films can be seen in Figure 5.

3.2. Visualisation of Interconnectivity

3.2.1 Shortest, intermediate and longest paths starting from a chosen surface pore

The shortest geodesic path in each of three leached EC/HPC films are visualised in Figure 6 (rendering made using Paraview (Ayachit, 2015)). The figure also shows one geodesic path from the intermediate category and one from the long category. The structure of the paths in the cross-sectional plane can be seen in the front views while the side views show the paths'

structure in the depth of the imaged volume. The tortuosity values, i.e. the relative lengths of the paths, for each film is summarised in Table 1 by yellow arrows. The outlet, where the paths have to end, is at the bottom.

The polymer film with the lowest porosity (HPC22) shows a different path structure compared to the other two. The shortest geodesic path in HPC22 is more than twice as long as the shortest geodesic paths found in HPC30 and HPC45, see Table 1. This is explained by the fact that shortest geodesic path of HPC22 is much more tortuous. The shortest geodesic paths in HPC30 and HPC45 have similar path structures. There is a difference between HPC30 and HPC45 when it comes to the tortuosity values. Higher weight percentage of HPC in the film results in less tortuous paths and lower tortuosity values.

For the intermediate and long geodesic paths, the path structure of HPC22 is again different from those of HPC30 and HPC45. For the higher porosity films, the intermediate and long geodesic paths are relatively straight passing through the point (marked with a black sphere) that defines the geodesic path. In contrast, the intermediate and longest geodesic paths of HPC22 take big detours and share a large portion of their paths towards the bottom of the film with the shortest geodesic path. This can be related to the percolation onset around 22% HPC discovered from previous studies performed on these types of films (Marucci et al., 2009). Since a smaller part of the film has been imaged in the z-direction, edge effects have to be considered. For a specific geodesic path, $\text{GeoPath}(p)$, a shorter path through the point p might have been found if the analysed porous network would have been larger in the z-direction. For similar reasons, edge effects also need to be considered for points p close to the boundaries. However, the geodesic paths in Figure 6 are not in direct contact with the boundaries and are therefore representative of the porous network.

3.2.2 Multiple short, intermediate and long paths

It is known from previous work that there is a percolation onset around 22 (weight/weight) of HPC (Marucci et al., 2009). The degree of the interconnectivity is visualised in Figure 7 by randomly choosing 40 of the short, intermediate and long geodesic paths within the films HPC22, HPC30 and HPC45. The tortuosity values, i.e. the relative lengths of the geodesic paths, for each film are summarised in Table 2. The geodesic path lengths decrease as the porosity increases, and the difference between HPC22 and HPC30 is larger than the difference between HPC30 and HPC45. Those 40 geodesic paths give an overview of the variability among paths through the porous networks. It can be seen from the 3D reconstructions that the

geodesic paths in HPC22 are a lot more tortuous than HPC30 and HPC45, and it is a general trend that higher porosity leads straighter geodesic paths. Also, all geodesic paths computed in HPC22 pass through either one of two parts of the pore space (highlighted in yellow in Figure 7). One reason for why the paths are more tortuous in HPC22 is that this pore network is more inhomogeneous in the sense that parts of HPC22 around the highlighted areas are poorly connected. More details about these highlighted areas are given in the next section.

Interestingly, even though the interconnectivity in HPC22 is much lower than in the other two films, the tortuosity scales in a similar way within each film. Consequently, comparing the lower bounds on the tortuosity intervals shown in Table 2, the lower bound for intermediate paths divided by the lower bound for long paths are 0.74, 0.71 and 0.75 for HPC22, HPC30 and HPC45, respectively; the lower bound for short paths divided by the lower bound for long paths are 0.61, 0.59 and 0.66 for HPC22, HPC30 and HPC45, respectively.

Since we are looking at a relatively small part of the whole EC/HPC film, we also need to consider if the size of the sample is large enough to provide results that are representative for the whole film. The size of a large enough sample is often referred to as a representative volume element (RVE). One method of determining an RVE is to use nested windows with increasing size and quantify the pore structure in each window (Chiu et al., 2013, Ch. 6.4.6). One method of determining an RVE is to use nested windows with increasing size and quantify the pore structure in each window (Chiu et al., 2013, Ch. 6.4.6), as is done e.g. in Aslannejad et al. (2017) and Barman et al. (2019). The 3D data presented in our work correlates very well with previous studies performed on phase-separated polymer films of EC/HPC. Due to our thorough 3D data acquisition on several samples per HPC concentration we have observed that these characteristic structural features in the films are representative for the whole films.

3.2.3 Quantification of channels

The data analysis method was used to quantify channels, i.e. parts of the porous network where paths coincide, in all three polymer films, see Table 3 and Figure 8. Interestingly, there seems to be a limiting layer in the lower portion in the HPC22 film where there are only two main channels, see yellow shaded area in Figure 8. The quantitative information in Figure 8 for HPC22 indicates that the channel to the right is much more prominent than the channel to the left. 97% of the paths, i.e. over 9 700 of the total 10 000 computed paths, pass through the right channel. The rest of the computed paths pass through the left channel. Note that all geodesic paths in Figure 7 pass through these two channels. In fact, the same two channels are obtained regardless of which pore at the top is chosen as inlet. A possible explanation for this limiting

layer is that HPC22 is close to the percolation onset. As the percolation onset is where the HPC starts to be fully connected, HPC22 could have isolated areas of HPC through which there are no or few paths.

In contrast, the prominent channels in HPC30 and HPC45 are only found around the chosen inlet pore. The maximum channel strength values are found around the chosen inlet pore for HPC30 and HPC45. The maximum channel strength value for HPC45 is lower than for the other two films. This is because the chosen inlet pore in HPC45 is relatively large, so that not all geodesic paths start in the same place. Diffusive transport rates are lower if there are strong bottlenecks in the porous network. Previous methods capture bottleneck effects caused by variations in pore size between larger pores and smaller pore necks connecting the larger pores (Berg, 2012; Holzer et al., 2013). The channel measure captures central features of the network and can therefore indicate if there are bottlenecks caused by many paths converging in one pore, which is a different type of bottleneck that is not captured by the existing methods. Channels of highly varying strength, such as those found in HPC22, indicate bottlenecks. However, a prominent channel is not necessarily a bottleneck that limits diffusive transport. A prominent channel with a large pore size would not slow down diffusive transport through the porous network. In HPC22, the pore size does not vary significantly and therefore the presence of the prominent channel is an indication of a bottleneck effect in the limiting layer.

In addition to the pore size, it is also important to consider alternative pathways that are possible, though slightly longer, through the porous network. These longer paths might not be taken into account by the channel measure, since the channel measure is computed from geodesic, i.e. shortest, paths. The longer paths around the prominent channel could still be used for transport in which case the prominent channel would not be a diffusive bottleneck, i.e. a structural feature limiting the transport. Even so, the geodesic channel measure indicates that the prominent channel in HPC22 has some limiting effect on diffusive transport since the pores connecting the porous network above the limiting layer with the porous network below are not well distributed. If the connecting pores were better distributed, there wouldn't be only two main channels so far apart in the limiting layer. In fact, there are no paths through the limiting layer other than through the two main channels, even though there are other pores that are connected to both the top and bottom of the porous network.

4. Conclusions

In this work we visualise and quantify how 3D porous networks, reconstructed from experimental FIB-SEM data, are connected to a chosen inlet pore. A data analysis method based on geodesic paths has been used. The paths have been divided into categories by length, enabling a more detailed quantification and visualisation. The newly introduced geodesic channel measure has been used to obtain information about part of the porous network where many paths coincide. The presented data analysis method illustrates lengths of paths through the porous network as well as bottleneck effects. Both are important factors that determine transport rates. The method has been applied to high spatial resolution 3D images from three porous polymer films with different porosities used as models of films for controlled drug release.

The longest and most tortuous paths were found within the porous network in the film with lowest porosity, where the phase-separated system is close to a percolation onset. The tortuosity was significantly lower in the other two films and decreased with increasing porosity and pore sizes. Finally, a limiting layer with channels of high channel strength was found in the low porosity film. The channels in the other two films were of lower channel strength and were more evenly distributed. This indicated that the interconnectivity in the film with the lowest porosity was significantly lower compared to the other two films. The lower interconnectivity should reduce the diffusive transport rate in the low porosity film.

3D visualisation is an important complement to summary statistics, such as mean values of different pore measures, since very different porous networks could have identical summary statistics. Exploring the porous networks using 3D visualisation allowed us to find important structural features, such as the inhomogeneity and limiting layer in the low porosity film.

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Appendix

A.1 Different inlet pore

As a complement to the quantification presented in Section 3.2.2 and Section 3.2.3, here corresponding results are given for an inlet pore chosen at the bottom of the porous network.

A.1.1 Multiple short, intermediate and long paths

Figure A.1 shows 40 randomly chosen paths from the short, intermediate and long categories of geodesic paths within HPC22, HPC30 and HPC45 (compare with Figure 7, Section 3.2.2). The tortuosity values for each film are summarised in Table A.1 (compare with Table 2, Section 3.2.2). As was found for the data presented in Figure 7 and Table 2, the tortuosity values decrease with increasing porosity. There is also a qualitative difference between the geodesic paths within HPC22, which are highly disorganized, and the paths within HPC30 and HPC40, which follow a clear trend when comparing paths from the short, intermediate and long categories.

All geodesic paths through HPC22 pass through the two yellow highlighted areas, just as in Figure 7. These areas correspond to the two main channels in the limiting layer which were identified in Section 3.2.3.

A.1.2 Quantification of channels

In Figure A.2, the geodesic channel strength with the inlet chosen at the bottom of the porous network are presented (compare with Figure 8, Section 3.2.3). The same limiting layer as was found in Figure 8 is also found in Figure A.2, with only two main channels through which all paths pass through. The channel strengths are summarised in Table A.2 (compare with Table 3, Section 3.2.3). As the inlet pore for the channel strength in Figure A.2 was chosen in the left part of the porous network, the main channel in the right part of the limiting layer has a lower channel strength in Figure A.2 compared to in Figure 8. However, even though the inlet pore was chosen in the left part, the main channel in the right part of the limiting layer has a higher channel strength than the main channel in the left part of the limiting layer. This indicates that the left part of the porous network is more poorly connected than the right part of the porous network.

535 **List of Figures and Tables with captions**

536
537 Figure 1. Illustration of geodesic paths, $\text{GeoPath}(p)$ (marked in red), for different points p
538 (marked in blue). The inlet (top) and outlet (bottom) are marked in the top of the figure. L is
539 the height of the porous network.

541
542 Figure 2. Illustration of geodesic channels, computed from 3000 $\text{GeoPath}(p)$ with the same
543 inlet and outlet as in Figure 1. The colourbar indicates the strength of the geodesic channel.
544 Only pores that are connected to both inlet and outlet are visible.

Figure 3. SEM images of cross section surface of leached a) HPC22, b) HPC30 and c) HPC45, where the porous network can be seen. The dark areas correspond to deep pores, the intermediate-intensity areas to the solid EC and the bright areas to shallow pores.

Figure 4. 3D reconstructions of the porous networks of the 3 studied films, a) HPC22 b) HPC30 and c) HPC45. The rigid porous EC backbone structure is coloured black, white surfaces illustrate the hollow pores.

Figure 5. Spherical pore size distribution for the three polymer films with different porosities. The spherical pore size distribution for HPC22 (blue line) has a peak around the median pore size 0.35 μm , whereas for HPC30 (red line) at 0.60 μm and for HPC45 (yellow) at 0.72 μm .

Figure 6. 3D visualisation of the shortest (black), an intermediate (blue) and a long (red) geodesic path, $\text{GeoPath}(p)$, with the points p shown as black spheres. The images to the left show the FIB-SEM cross-section surface and the images to the right show the paths from the side. The inlets, where the paths have to start, are marked in black and indicated with grey arrows. The outlet, where the paths have to end, is at the bottom.

Figure 7. 3D visualisation of 40 randomly chosen short, intermediate and long geodesic paths in HPC22, HPC30 and HPC45. The inlet pore is marked in black at the top and is indicated with a grey arrow, and the outlet is at the bottom of the porous network. The points p that define the paths are shown as black spheres. Two parts of the pore space in HPC22 are marked in yellow. All computed geodesic paths pass through one or the other of these two parts.

Figure 8. 3D Visualisation of geodesic channel strength for HPC22, HPC30 and HPC45, with the chosen inlet at the top. The colour scale is the same for all three images where red corresponds to high channel strength and blue to low channel strength. The opacity is low for channels of low channel strength. In HPC22, a limiting layer is marked with a yellow shaded area.

Table 1.

The relative path lengths (tortuosity) for the geodesic paths through the leached EC/HPC films shown in Figure 6.

Tortuosity / Film	HPC22	HPC30	HPC45
Shortest geodesic path	2.29	1.16	1.08
Intermediate geodesic path	2.93	1.44	1.35
Long geodesic path	3.83	2.01	1.84

Table 2. Summary of the tortuosity intervals for each of the categories of geodesic paths (short, intermediate and long) in HPC22, HPC30 and HPC45, with the inlet chosen at the top as shown in Figure 7. The tortuosity values in the brackets represent the lowest and highest tortuosity values from each category.

Tortuosity / Film	HPC22	HPC30	HPC45
Short geodesic paths	[2.29 2.55]	[1.16 1.25]	[1.08 1.15]
Intermediate geodesic paths	[2.79 3.16]	[1.39 1.65]	[1.23 1.38]
Long geodesic paths	[3.76 5.20]	[1.96 2.90]	[1.64 2.38]

Table 3. Summary of the geodesic channel measure for HPC22, HPC30 and HPC45, with the inlet at the top. The maximum, mean and standard deviations computed from channel strength values larger than zero are shown.

Channel strength / Film	HPC22	HPC30	HPC45
Max value	0.97	1.00	0.56
Mean value	0.023	0.009	0.007
Standard deviation	0.08	0.03	0.02

Appendix list of Figures and Tables with captions

Figure A.1. 3D visualisation of 40 randomly chosen short, intermediate and long geodesic paths in HPC22, HPC30 and HPC45. The inlet pore is marked in black at the bottom and is indicated with a grey arrow, and the outlet is at the top of the porous network. The points p that define the paths are shown as black spheres. Two parts of the pore space in HPC22 are marked in yellow. All computed geodesic paths pass through one or the other of these two parts.

659 Table A.1. Summary of the tortuosity intervals for each of the categories of geodesic paths
 660 (short, intermediate and long) in HPC22, HPC30 and HPC45, with the inlet chosen at the
 661 bottom as shown in Figure A.1. The tortuosity values in the brackets represent the lowest and
 662 highest tortuosity values from each category.

Tortuosity / Film	HPC22	HPC30	HPC45
Short geodesic paths	[2.74 2.96]	[1.17 1.27]	[1.09 1.17]
Intermediate geodesic paths	[3.09 3.26]	[1.45 1.70]	[1.27 1.45]
Long geodesic paths	[3.51 4.87]	[2.00 2.90]	[1.74 2.62]

667

668
 669 Table A.2. Summary of the geodesic channel measure for HPC22, HPC30 and HPC45, with
 670 the inlet chosen at the bottom. The maximum, mean and standard deviations computed from
 671 channel strength values larger than zero are shown.

Channel strength / Film	HPC22	HPC30	HPC45
Max value	1.00	1.00	0.72
Mean value	0.032	0.012	0.008
Standard deviation	0.11	0.03	0.02