

STEREOLOGICAL–FRACTAL ANALYSIS AS A TOOL FOR A PRECISE DESCRIPTION OF THE MORPHOLOGY OF HYBRID ALGINATE MEMBRANES*

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A precise description of the morphology of a material is necessary in order to establish structural and functional relationships. Tools for morphological analysis should be quantitative techniques, which would yield objective and reproducible values for any morphological structure and enable statistically defined comparisons. The combination of the stereological analysis and fractal analysis provides the researchers with such a tool. This work investigated hybrid alginate membranes filled with various amount of magnetite (Fe_3O_4) and crosslinked using four different agents, *i.e.* calcium chloride (AlgCa), phosphoric acid (AlgP), glutaraldehyde (AlgGA) and citric acid (AlgC). Alginate membranes can be used to dehydrate ethanol in the process of pervaporation. The morphology of studied membranes was characterized on the basis of the image analysis of the membrane cross sections obtained from a scanning electron microscope Phenom Pro-X. The quantitative analysis of the structure and morphology of the above-named materials was conducted by using a new tool: stereological–fractal analysis (the so-called SFA method). The SFA method was based on the shape descriptors (elongation factor, surface factor, irregularity parameter and bulkiness), fractal dimension, generalized fractal dimension and lacunarity. In relation to the membranes subjected to the tests, it was possible to identify the correlation between transport properties (pervaporation separation index (PSI)) and morphological parameters. The use of a comprehensive analysis made it possible to determine the morphology of the membrane with the best separation properties.

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1. Introduction

In recent years, fast development of membrane technologies has been observed. The main advantages of membranes applications are: low energy and chemical consumption, easy scale enlargement as well as automation and compactness of installation [1, 2]. The use of membranes and membrane processes in various branches of industry is currently one of the most dynamically developing research areas. It is connected with the intensive development of materials science, which gives the possibility to design materials, in particular, membranes with specific properties [1, 3]. Modern trends in this field include hybrid materials (consisting of organic and inorganic components) such as membranes created by adding inorganic particles to organic polymer structures (matrices). The growing interest in modern polymer materials means that the development of methods for assessing the structure and morphology of polymeric materials constitutes a current and important scientific issue [1, 2]. The above-mentioned methods have to take into account the complex chemical structure of polymers and predict the ensuing properties of plastics on the basis of their internal structure. The information about the structure–properties relationship lays the foundations for the designing process of new materials in order to obtain desirable material features and applications.

This article constitutes a part of the project aiming at the development of membranes of predefined transport properties. Previous articles within this scope focused on the manufacturing of different types of hybrid membranes as well as measurements of their pervaporation properties [4, 5]. From the very beginning of the research, the authors observed a distinct relationship between the membrane properties and its structure. Due to this fact, it is essential to quantitatively describe the morphology of membranes in order to determine features responsible for certain physical, mechanical and transport properties. So far, the analysis of the morphology of hybrid membranes has been conducted by means of various tools, including stereological and fractal methods. The current work describes in detail a new tool which takes advantage of previously used methods and supplements them with lacunarity (the so-called SFA method). This paper presents the SFA (stereological–fractal analysis) as an extensive approach to the examination of the morphology of complex systems. It discusses both the advantages and limitations of the SFA method. Moreover, it shows the results obtained for hybrid alginate membranes as well as the relationship between membrane morphology and properties.

This paper has been divided into three sections. Section 2.1 treats of hybrid alginate membranes, their manufacturing, properties and application. Section 2.2 deals with the stereological–fractal analysis (SFA) being the new

tool for testing the morphology of complex systems. Section 3 presents the results of the SFA conducted for hybrid alginate membranes. The last part of the article contains the conclusions from the research.

2. Materials and methods

2.1. Membranes

The subject of the research encompassed hybrid alginate membranes filled with various amounts of magnetite and crosslinked using four different agents, such as calcium chloride (AlgCa), phosphoric acid (AlgP), glutaraldehyde (AlgGA) and citric acid (AlgC). In general, 1.5% sodium alginate solution was prepared by dissolving an appropriate amount of sodium alginate powder in deionised water. This solution was mixed with an appropriate portion of magnetite nanoparticles (from 0 to 25 wt%). The solution was then placed in an ultrasonic bath for precise mixing of ingredients. The sodium alginate solution was subsequently cast onto a levelled glass plate and evaporated to dryness at 40°C. After 24 h, each membrane was crosslinked using suitable crosslinkers, such as 2.5 wt% calcium chloride in water, 1.25 wt% glutaraldehyde solution in water, 3.5 vol.% of phosphoric acid or 3.5 wt% citric acid in an isopropanol/water mixture. Detailed information about the preparation of hybrid sodium alginate membranes and iron oxide nanoparticles had been presented in previous papers [4].

Pervaporation is a membrane separation technology applied especially for the dehydration of organic solvents [3]. As sodium alginate has excellent permselectivity towards water, it has been identified as a promising membrane material for the dehydration of ethanol. The pervaporation properties of membranes were investigated. The tests were carried out at room temperature and at the pressure equalling to 300 Pa on the permeate side. An aqueous solution of 97 wt% ethanol was used as the feed solution. The membrane (effective area of $112 \times 10^{-4} \text{ m}^2$) was placed in the cell where the feed solution was loaded. The permeate was condensed in a vacuum trap immersed in liquid nitrogen (-196°C). Flux was calculated from the measured weight of liquid collected in the cold traps during certain time intervals at a steady-state condition. The feed, permeate and retentate composition were analysed using gas chromatography on PerkinElmer Clarus 500 GC equipped with a 30 m elite-WAX ETR column and a flame ionization detector (FID) [4]. This experiment was repeated three times for all types of membranes. More extensive information on this subject can be found in preceding works [4, 5].

The pervaporation experiment enabled the authors to determine parameters which describe separation properties of the investigated membranes [3]. The first parameter was a composite parameter called pervaporation sepa-

ration index (PSI). In addition to that, two further parameters were used for the description of the separation properties of the membranes, namely separation factor (α_{AB}) and selectivity coefficient (Sc_{AB}). The former one was calculated by means of the following formula:

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B}, \quad (1)$$

where x_A, x_B — mean weight fraction of components in feed, y_A, y_B — mean weight fraction of components in permeate, whereas the latter one was equal to the ratio of permeability of separated components, as can be seen in the formula below

$$Sc_{AB} = \frac{P_A}{P_B}. \quad (2)$$

Between membrane permeability and selectivity there exists a trade-off. Due to this fact, the pervaporation separation index (PSI) has been widely accepted for the purpose of evaluation of the overall pervaporation performance.

It is defined as follows:

$$PSI = J(\alpha_{AB} - 1), \quad (3)$$

where J — means the total permeate flux, α_{AB} — is a separation factor. The permeation flux of component i is calculated using the following equation:

$$J_i = \frac{m_i}{A_{\text{eff}}t}, \quad (4)$$

where m_i — means the weight of component i in permeate, A_{eff} — is effective membrane area, t — is permeation time.

2.2. SFA tool

The analysis of complex systems requires the description of both the morphology of individual elements of the system and their mutual connections as well as the characterization of the structure as a whole. This work discusses a method that allows the analysis of microscopy images. The classical analysis of complex systems consists in determining a number, size, shape and distribution of elements (particles) in the image [6–8]. It enables the comparison of a one particular image to other available images. The size of elements in the image is closely related to their shape. Although every person can intuitively define the shapes of surrounding objects, in the image analysis this property is difficult to characterize due to the lack of an unambiguous definition. The basic difficulty in determining the shape is the size of a given object.

Whereas a big element can be precisely and correctly defined, a considerable reduction of its magnification results in the apparent alteration of its shape to human eye.

The modern image analysis omits this problem by means of the so-called shape factors, which are dimensionless (the value remains unchanged with the change of the object size). These parameters are sensitive to specific shape changes that may occur during the observed processes. Moreover, the above-mentioned parameters are easy to interpret using a reference point (*e.g.* a sphere, a circle, a rectangle) [9]. Such coefficients were calculated as the first parameters among others that may be computed in the SFA analysis. Figure 1 shows the dimensions which make it possible to define shape factors for any element. The construction of the rectangles with the smallest area around the particle profile enables the determination of mathematical descriptors of particle shapes. Therefore, if A is the projected area of an object and L is the actual perimeter of the profile, and a and b are the lengths of the sides of the minimum area of the embracing rectangle, then the following particle shape descriptors are obtained. The first parameter is elongation factor of the following formula:

$$f_1 = a/b \quad (5)$$

then, bulkiness equals

$$f = \frac{A}{ab} \quad (6)$$

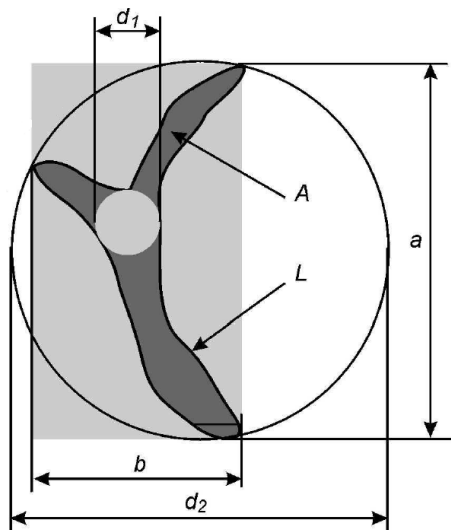


Fig. 1. The construction of the rectangles with the smallest area around the particle profile enables the determination of mathematical descriptors of particle shapes.

and surface factor (circularity) is

$$f_2 = \frac{L^2}{4\pi A}. \quad (7)$$

These parameters are also known as Hausner shape indices. Elongation factor determines the degree of elongation of the examined element in relation to a circle. Circularity for the circle is equal to 1, for other shapes its value is greater than 1. Another parameter is irregularity parameter f_3 , which is a coefficient both sensitive to profile irregularities and surface elongation. It is defined as follows:

$$f_3 = d_1/d_2, \quad (8)$$

where d_1 and d_2 are the diameters of the maximum inscribed and minimum circumscribed circles, respectively.

Next parameters of the SFA were based on fractal dimension d_f and generalized fractal dimension D_q , which are useful tools for quantifying the structure and morphology of self-similar objects or structures [10, 11]. Fractal dimension [12] is a measure of self-similar sets resulting from the relation of the scaling of a number of covers of a given object to the size of this particular cover

$$N(\epsilon) \sim \epsilon^{-d_f}. \quad (9)$$

Therefore, it can be defined in the following way:

$$d_f = \lim_{\epsilon \rightarrow 0} \frac{\ln N(\epsilon)}{\ln 1/\epsilon}, \quad (10)$$

where ϵ is a size of an element of the cover and $N(\epsilon)$ is a number of elements of the cover

Fractal dimension describes an object using only one value for this purpose. Since it is only the number of non-empty boxes that is added and summed up (without checking how much of the studied object is immersed in an individual box), it is possible to find different objects whose fractal dimension equals the same value. In order to specify the quantitative description of fractals more precisely with a view to their differentiation, a notion of a generalized dimension was introduced by means of the following formula:

$$D_q = \frac{1}{q-1} \lim_{\epsilon \rightarrow 0} \frac{\ln \sum_{i=1}^{N(\epsilon)} P_i^q}{\ln \epsilon}, \quad (11)$$

where q is a real number, ϵ is a size of an element of the cover, P_i is a probability of finding a point in a given element of the cover and $N(\epsilon)$ is a

number of elements of the cover. Generalized dimension makes it possible to characterize an object by means of an infinite quantity of numbers. These numbers create a set which is called a multifractal spectrum. It includes numerical values which describe structural elements of the object, groups of such elements and their mutual relation. For instance, for $q = 0$, fractal dimension D_0 (previously d_f) is obtained. This dimension is responsible for scaling mass. The higher it gets, the denser the object is. Multifractal spectra are most often presented in a graphic form as a function D_q . In order to facilitate the analysis and comparison of the spectra, function D_q is converted by means of Legendre's transformation in the form of function $f(\alpha)$

$$f(\alpha) = \alpha q - \lim_{\epsilon \rightarrow 0} \frac{\ln \sum_{i=1}^{N(\epsilon)} P_i^q}{\ln \epsilon}, \quad (12)$$

where α — new index of dimension (after Legendre's transformation performed for D_q) [13]. The degree of multifractality ΔD is related to the deviation from simple self-similarity and constitutes the difference between the maximum dimension and minimum dimension associated with the least dense and most dense points in the sets, as shown in this formula

$$\Delta D = D_{-\infty} - D_{+\infty}. \quad (13)$$

In order to determine fractal dimension/generalized fractal dimension, a Box-Counting Method (BCM) is widely used. It consists in the covering of a given object with a mesh of a particular size ϵ and counting non-empty boxes depending on the inverse of a reduction factor [11, 14–16]. The last parameter in the SFA analysis was lacunarity which measures in what way patterns, especially fractals, fill space. The analysis of lacunarity is the analysis of empty spaces of a material subjected to a test on the basis of the spatial distribution of data sets [17, 18]. This analysis adopted an algorithmic method of the so-called “sliding box” as the primary test method [17]. The “sliding box”, having dimension of size $s \times s$, is located at the top left-hand corner of the map. The number of occupied places in the box is defined as the hole area M . The box is moved by one column to the right and the area of the box is calculated again. The above-presented process is repeated in all rows and columns. Next, the frequency of mass distribution of box $n(M, s)$ and, afterwards, the probability of distribution $Q_n(M, s)$ is determined. Moments of distribution are defined as follows:

$$Z_{Q_n}^{(q)}(s) = \sum_{M=1}^{s^2} M^q Q_n(M, s), \quad (14)$$

where M is a number of bright points (the area of the hole), s is a mesh size (the size of the “sliding box”) and $Q_n(M, s)$ is a function of probability

density in relation to elements of the mesh having radius s and mass M . Afterwards, using the first and the second moment, it is possible to determine lacunarity

$$A(s) = \frac{Z_{Q_n}^{(2)}(s)}{\left[Z_{Q_n}^{(1)}(s)\right]^2}. \quad (15)$$

On the basis of formula (15), it is possible to state that lacunarity is first of all the function of the following parameters: the size of “sliding box”, the geometry of a system subjected to investigation or the distribution of the map fraction. If the dimensions of the box increase, the mean surface area of the empty spaces in the box grows as well [19, 20]. The SFA method combines three various tools that were previously usually used separately. Therefore, this method makes it possible to describe more precisely and accurately the unique features of the investigated structure.

3. Results

The morphology of the studied membranes was characterized on the basis of the image analysis of the membrane’s cross section obtained from a scanning electron microscope Phenom Pro-X. In order to get consistent results, the SEM images were taken from at least five different areas representative of all types of membranes. Figure 2 presents examples of scanning electron microscope images of the analysed materials. On the basis of these images, the stereological–fractal analysis was conducted.

As it was shown previously, the size of a single particle ranges between 10–20 nm [5]. To quantify the differences between individual grain shapes, the shape factors described in Section 2.2 (*i.e.* elongation factor (f_1), bulkiness (f), surface factor (f_2) and irregularity parameter (f_3)) were determined. In all cases, the values of the respective shape factors were calculated for all powder grains contained in the polymer matrix and the results were averaged.

Elongation factor (f_1) adopted values from 1.04 to 3.57. Its value was greater than one, which means that the grains of magnetic powder are irregular and elongated. The larger factor f_1 , the longer elongation of the grain. However, their shape is not rectangular, which can be deduced from the value of bulkiness f .

Surface factor f_2 determines to what extent the shape of grains is close to the circle (f_2 for the circle equals 1). In this case, it turned out that the objects showed a large dispersion, and the circular ones were extremely rare. The average values of this coefficient ranged from 0.38 to 1.00, while the

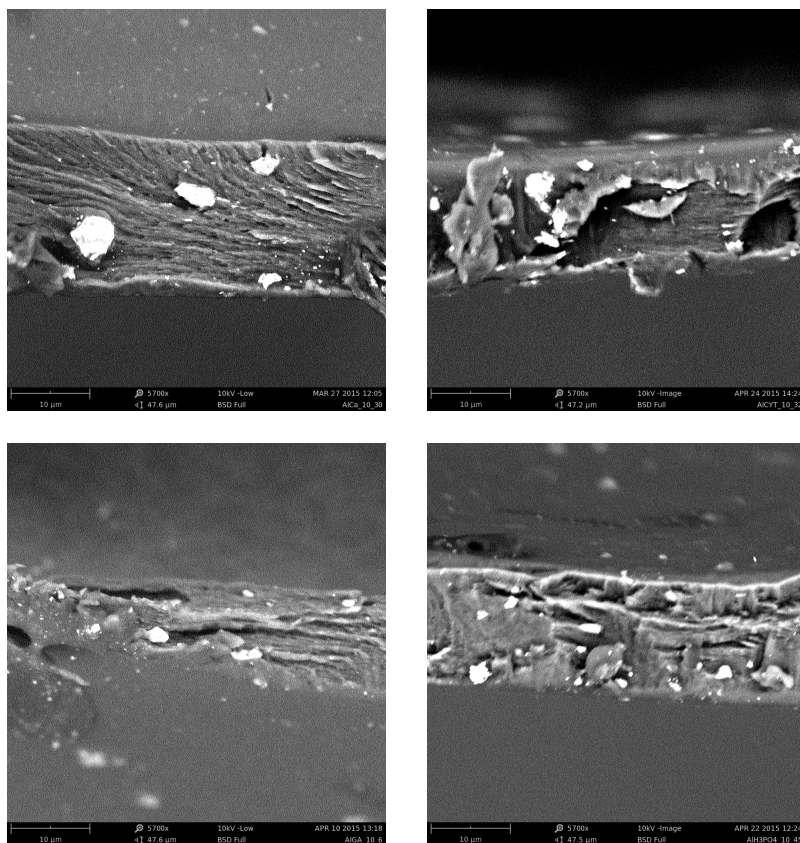


Fig. 2. Images of the cross section of alginates membrane modified by calcium ions (top left), citric acid (top right), glutaraldehyde (bottom left) and phosphoric acid (bottom right) with addition of magnetic powder Fe_3O_4 .

values of irregularity parameter (f_3) ranged from 1.20 to 4.29. Coefficients larger than 1 indicate that the shape of the grains is not perfectly spherical, but elongated and irregular.

The values of selected coefficients are given in Table I. The presented results indicate that the grains of magnetic powder in the analysed membranes do not take the shape described in the Euclidean geometry, but show irregularity. The analysis based on f_1 , f_2 , f_3 and f allowed for a quantitative description of the shape of particles, but did not show a clear variation in the morphology between individual membranes.

During this part of the analysis, it was also observed that the shape of magnetite particles is not perfectly spherical, but elongated and irregular. Moreover, they have a similar distribution in the polymer matrix forming mainly four aggregates: 40 nm, 250 nm, 450 nm and several μm in diameter.

TABLE I

Results obtained from stereological analysis.

Type of membrane	f	f_1	f_2	f_3
AlgCa (Fe ₃ O ₄ 5%)	0.38–1.00	1.20–2.08	1.00–3.51	1.22–2.43
AlgCa (Fe ₃ O ₄ 15%)	0.38–1.00	1.05–2.53	1.00–3.51	1.51–2.57
AlgCa (Fe ₃ O ₄ 25%)	0.38–1.00	1.05–2.17	1.00–3.51	1.48–2.26
AlgP (Fe ₃ O ₄ 5%)	0.38–1.00	1.04–1.79	1.00–3.51	1.20–1.79
AlgP (Fe ₃ O ₄ 15%)	0.38–1.00	1.33–2.40	1.00–3.51	1.43–2.75
AlgP (Fe ₃ O ₄ 25%)	0.38–1.00	1.10–1.91	1.00–3.51	1.30–2.04
AlgGA (Fe ₃ O ₄ 5%)	0.50–1.00	1.13–2.80	1.00–2.54	1.33–3.37
AlgGA (Fe ₃ O ₄ 15%)	0.50–1.00	1.06–2.64	1.00–2.54	1.33–3.16
AlgGA (Fe ₃ O ₄ 25%)	0.38–1.00	1.08–2.07	1.00–3.51	1.18–2.37
AlgC (Fe ₃ O ₄ 5%)	0.38–1.00	1.09–1.59	1.00–2.54	1.13–1.96
AlgC (Fe ₃ O ₄ 15%)	0.38–1.00	1.11–1.65	1.00–3.51	1.20–2.32
AlgC (Fe ₃ O ₄ 25%)	0.50–1.00	1.13–2.83	1.00–3.51	1.43–4.29

Figure 3 shows an example of an SEM picture (magnification 8700 $\times$) in which three different size classes of aggregates have been marked. The aggregates with a size of a few micrometres are also clearly visible on it.

The above-mentioned aggregates are often placed near the surface of the membranes, and only a small number is located in the middle part of the membranes (crosslinking with calcium ions, orthophosphoric acid, glutaraldehyde with the addition of 5–20% powder and citric acid with the addition of 5% and 10% powder). In some cases, grains were dispersed in the membrane, whereas larger ones were located near the membrane surface (crosslinking with calcium ions, orthophosphoric acid, glutaraldehyde with the addition of 25% powder and citric acid with the addition of 15–25% powder).

The next part of the analysis was concerned with the description of the distribution of particles and aggregates in the polymer matrix. It was found that the resulting structure was self-similar. Therefore, the fractal dimension and multifractal spectrum were determined.

Table II shows the values of generalized fractal dimension for examined membranes. The fractal dimension ranged from 2.65 to 2.76 and indicated self-similar structure of membranes. Multifractal spectra were characterized by large width, that is D_q was less than 8 and greater than 2. This shows the inhomogeneity of the structure, which resulted from the stochastic self-similarity. The stochastic self-similarity in turn resulted from the irregular

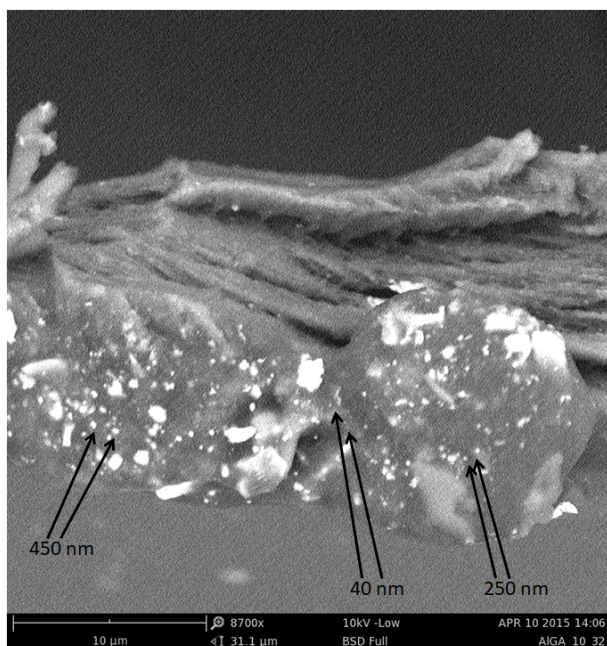


Fig. 3. SEM image of the cross section of alginate membrane modified by glutaraldehyde with addition of 15% magnetic powder Fe_3O_4 .

distribution of magnetic powder in the membranes. It should be emphasized that in the case of deterministic or, in other words, ideal self-similarity, the value of ΔD equals 0. Figure 4 presents results in the form of multifractal spectra. The chart of the collective curves D_q from q shows that the graphs overlap for q greater than 0, however, for q less than 0, the curves differ from one another.

This fact of overlapping can be even better observed in the $f(\alpha)$ chart. In contrast to the left branches, the right branches of the graphs do not overlap.

Both charts show that the amounts and sizes of the smallest powder grains in the polymer matrix are similar for all membranes (overlapping of some parts of the curves), whereas the numbers and sizes of aggregates are different for various types of membranes (hence, the respective parts of the curves do not overlap).

The last one parameter obtained within the framework of the SFA was lacunarity. Averaged results were presented in the chart in figure 5. The results were similar for the majority of analysed objects. The lacunarity method does not allow distinguishing between membranes in such a good way as the analysis based on the generalized fractal dimension. The solely

TABLE II

Results obtained from fractal analysis based on generalised fractal dimension.

Type of membrane	d_f	D_1	D_2	ΔD	$D_0-D_{+\infty}$	$D_{-\infty}-D_0$
AlgCa (Fe ₃ O ₄ 5%)	2.69	2.48	2.45	4.87	4.49	0.38
AlgCa (Fe ₃ O ₄ 10%)	2.72	2.56	2.51	4.78	4.31	0.47
AlgCa (Fe ₃ O ₄ 15%)	2.71	2.52	2.49	4.70	4.19	0.51
AlgCa (Fe ₃ O ₄ 20%)	2.65	2.43	2.37	4.73	3.89	0.84
Ca (Fe ₃ O ₄ 25%)	2.71	2.53	2.48	4.81	4.33	0.48
AlgP (Fe ₃ O ₄ 5%)	2.71	2.54	2.50	4.68	4.22	0.46
AlgP (Fe ₃ O ₄ 10%)	2.73	2.59	2.56	4.56	4.22	0.34
AlgP (Fe ₃ O ₄ 15%)	2.74	2.57	2.55	4.52	4.19	0.33
AlgP (Fe ₃ O ₄ 20%)	2.73	2.58	2.55	4.58	4.03	0.55
AlgP (Fe ₃ O ₄ 25%)	2.69	2.50	2.45	4.81	4.22	0.59
AlgGA (Fe ₃ O ₄ 5%)	2.69	2.49	2.46	4.86	4.32	0.54
AlgGA (Fe ₃ O ₄ 10%)	2.73	2.56	2.54	4.92	4.52	0.40
AlgGA (Fe ₃ O ₄ 15%)	2.76	2.64	2.60	4.94	4.57	0.37
AlgGA (Fe ₃ O ₄ 20%)	2.71	2.52	2.48	4.89	3.26	0.63
AlgGA (Fe ₃ O ₄ 25%)	2.69	2.49	2.43	4.90	4.40	0.50
AlgC (Fe ₃ O ₄ 5%)	2.70	2.52	2.47	4.82	4.23	0.59
AlgC (Fe ₃ O ₄ 10%)	2.70	2.51	2.47	4.77	4.31	0.46
AlgC (Fe ₃ O ₄ 15%)	2.72	2.54	2.50	4.76	4.22	0.54
AlgC (Fe ₃ O ₄ 20%)	2.72	2.57	2.54	4.63	4.21	0.42
AlgC (Fe ₃ O ₄ 25%)	2.72	2.58	2.55	4.70	4.35	0.35

used lacunarity method does not allow to distinguish various type of membranes. However, the values obtained for three kinds of membranes were significantly higher than in other cases. It can be stated that the more homogenous the structure, the lower values of lacunarity. As a result, in these three cases, the holes (filled in by particles and aggregates) in the polymer matrix revealed a different distribution than in the remaining membranes.

The results from SFA were compared with the separation properties of tested membranes. Mainly the relationship between the separation properties described by PSI was analysed. Relation between pervaporation separation index (PSI) and the degree of self-similarity ΔD is presented in figure 6. This relationship is linear. The membranes with the highest self-similarity have better separation properties.

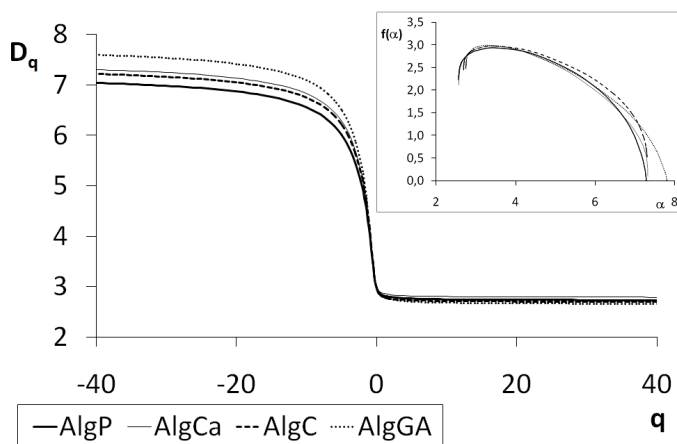


Fig. 4. Generalised fractal dimension in the form of D_q versus q and in the form of spectrum $f(\alpha)$.

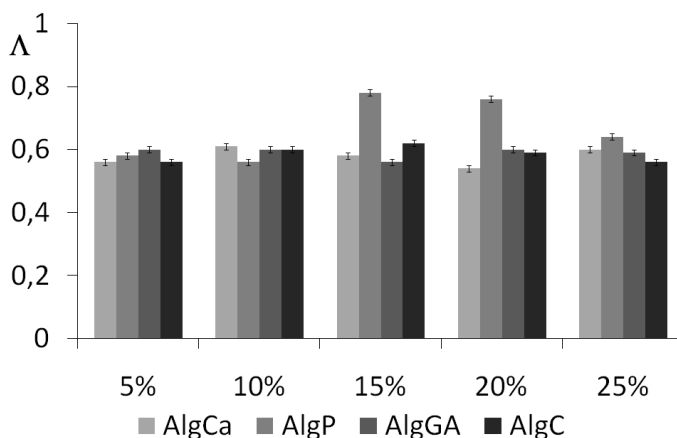


Fig. 5. Values of lacunarity for hybrid alginate membranes.

In the next step, it has been checked whether it is possible to correlate separation properties with lacunarity. In this case, no such linear relationship was found. Membranes crosslinked by phosphoric acid containing 15% and 20% of magnetic powder were also distinguished from others like in figure 6 by a much higher value of lacunarity (Fig. 7).

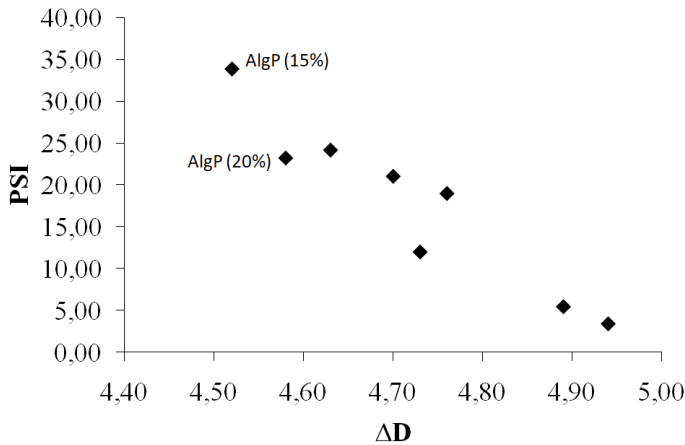


Fig. 6. Relation between pervaporation separation index PSI and degree of self-similarity ΔD for exterminated hybrid alginate membranes.

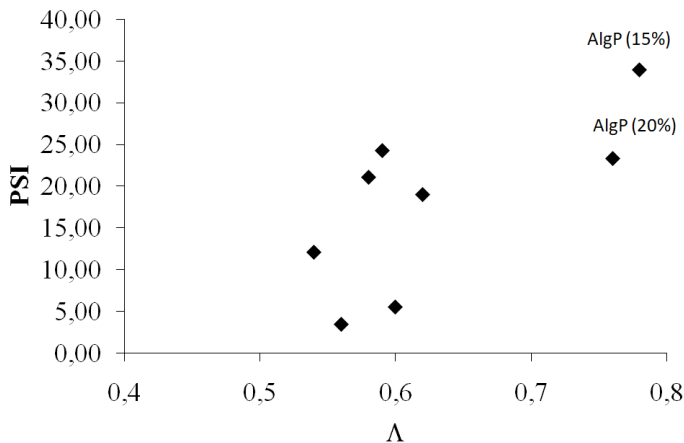


Fig. 7. Relation between pervaporation separation index PSI and lacunarity Λ for exterminated hybrid alginate membranes.

4. Concluding remarks

All the results obtained within the stereological–fractal analysis served the purpose of complete characteristics of each type of the investigated membranes. It had already been stated in the previous works that in relation to the membranes subjected to the tests, it was possible to identify the linear correlation between pervaporation separation index (PSI) and the degree of self-similarity ΔD . All results indicate that the membranes of the highest self-similarity are also characterized by the highest separation properties.

When the degree of self-similarity ΔD reaches a minimum, the pervaporation separation index is the highest. Self-similarity is not synonymous with homogeneity of the structure. Self-similarity consists in the fact that a shape of the whole object is similar to a shape of a fragment (or several fragments) of this object. This means that there are the same structural elements in the set but on a different scale. Membranes standing out among all membranes subjected to analysis were the membranes crosslinked using phosphoric acid with a 15% and 20% addition of magnetic powder. The structures of the above-named membranes are characterized by the lowest values ΔD which indicate that they are more self-similar than the remaining membranes. At the same time, the values of lacunarity are the highest, which proves that identical elements on a different scale are placed in a heterogenic way in the polymer matrix. These membranes show the best ethanol dehydration effectiveness.

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