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## PREPARATION AND CHARACTERIZATION OF MIXED-MATRIX-MEMBRANES

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## PRZYGOTOWANIE I CHARAKTERYSTYKA MEMBRAN WIELOMATRYCOWYCH

### Abstract

In the concept of mixed-matrix-membrane (MMM) producing, rubbery polymer PDMS and a micro porous carbon adsorbent have been chosen as membrane components. Transport properties of MMMs strongly depend on the polymer and filler interface. Blockage of the carbon pores by polymer chains eliminates the necessary mass transfer. As a fundamental step in preparation pore blockage was investigated for different carbon treatments. Polymer penetration into the pores was analysed by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX). By using saturation method of carbon particles with a solvent pore blockage with silicon chains was hindered partly.

*Keywords: mixed-matrix-membranes, PDMS, pore blockage, EDX*

### Streszczenie

Jako składniki membrany w koncepcji wytwarzania membran wielomatrixowych (MMM) wybrano polimer gumy PDMS oraz mikroporowaty adsorbent węgla. Właściwości MMM w zakresie przenoszenia zależą w dużej mierze od obszaru wzajemnego oddziaływania polimeru i materiału wypełniającego. Blokada porów węgla za pomocą łańcuchów polimerowych eliminuje konieczność przenoszenia masy. Blokada porów została potraktowana jako najważniejszy etap przygotowań pod kątem poddawania węgla działaniu różnych środków. Przenikanie polimerów do porów przeanalizowano w ramach mikroskopii elektronowej skaningowej (SEM) oraz rentgenowskiej spektroskopii energii dyspersyjnej (EDX). Zastosowanie metody saturacji cząsteczek węgla z rozpuszczalnikiem pozwoliło częściowo powstrzymać blokadę porów z łańcuchami krzemu.

*Słowa kluczowe: membrany wielomatrixowe, PDMS, blokada porów, EDX*

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## 1. Introduction

Gas separation has become a major industrial application of membrane technology since past 25 years. As energy costs rise, it has been playing an increasingly important role in reducing the environmental impact and costs of industrial processes [1, 2]. Gas separation membranes offer a number of benefits over other gas separation technologies since they do not require a phase change in the separation process which means additional significant energy costs. Additionally, gas separation membrane units are smaller than other types of plants; therefore they have relatively small footprints. Currently, gas separation membranes are most widely used in industry for oxygen and nitrogen enrichment, hydrogen-hydrocarbon separation, nitrogen separation from air, CO<sub>2</sub> removal from natural gas, organic vapor removal from air or nitrogen streams [3].

The most widely used membrane materials for gas separation are polymers [4]. They are attractive as membranes because they can be processed into hollow fibers with high specific surface areas. Ideally, membranes should exhibit high selectivity and high permeability. In some cases, the membrane materials, membrane configuration, and preparation routes are inadequate to fully exploit new industrial fields. In 1991 Robeson plotted selectivity versus permeability for many polymeric membranes with respect to a specific gas pair. He reported that a general trade-off exists between permeability and selectivity [5]. The trade-off is one of the biggest problems faced by pure polymeric membranes which mostly limits their economical applications in industries [6]. In view of this situation, a new approach is needed to enhance separation properties of membranes and to produce cost-effective and defect-free membranes above the upper bound.

## 2. Mixed Matrix Membranes (MMMs)

The latest membrane morphology is mixed-matrix-membranes (MMMs) consisting of organic polymer and inorganic particle phases [3]. The continuous phase is typically a polymer and the dispersed phase consists of inorganic particles; like zeolite, carbon molecular sieves, or nano-size particles (Fig. 1). MMMs have the potential to achieve higher se-

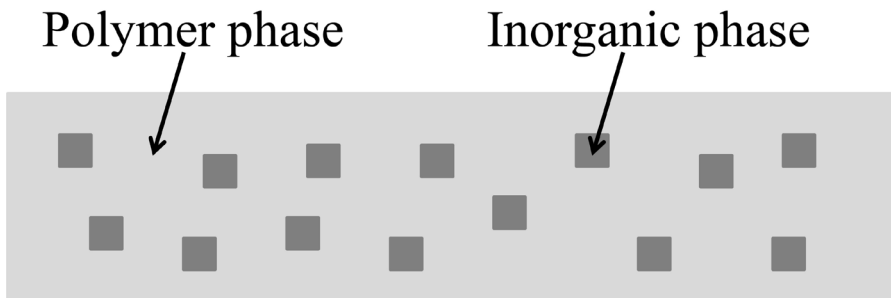


Fig. 1. Schematic of MMM

Rys. 1. Schemat MMM

lectivity, permeability, or both compared to the existing pure polymeric membranes, by the addition of the inorganic particles with their inherent superior separation characteristics.

When these highly selective porous fillers are added to the polymer matrix, this increases not only the permeability of the desired component but also the overall selectivity. Robeson reviewed the upper bound with the latest available data in 2008 and he reported that many studies with the MMM approach exceeded upper bound behavior [7].

Most research related to form a MMM, generally followed a procedure as; (1) preparation of membrane materials; polymer solution and pre-treatment of inorganic filler, (2) mixing polymer solution and filler, (3) casting these mixture onto a support structure, and (4) drying of prepared MMMs as a post-treatment step [8, 9]. One of the major difficulties experienced in preparation of MMMs is pore blockage of inorganic fillers by the polymer chains resulting in low selectivity when they are mixed [3]. Depending on the pore size of inorganic fillers, the polymer chain can fill the pores in various degrees [2]. The inorganic filler could be completely excluded from the transport process as a result of filling by the polymer chains; therefore, no improvement in performance could be obtained. On the other hand, the blockage may narrow a part of the pores. Since blockage of the pores by polymer chains may completely eliminate the function of the inorganic filler, investigations are necessary to suppress this effect.

In this work, as a crucial point of successful MMM preparation, pore blockage was investigated. Activated carbon as filler was saturated with a solvent before mixing with polymer solution. Pore blockage of saturated and unsaturated carbon particles was compared and the influence of the solvent-saturation process on pore blockage was observed. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) techniques were applied to determine quantitatively pore blockage degree.

### 3. Experimental

#### 3.1. Materials

##### 3.1.1. Polymer solution

Polydimethylsiloxane (PDMS) was selected as continuous phase. PDMS is a solubility-selective rubbery silicone historically and still largely used in composite membranes [4]. Polymer precursor solution (PDMS, 30 wt.%) was diluted with solvent and stirred magnetically at 400 rpm for 30 min at room temperature. Then, it was mixed with cross-linking agent (5 wt.%) and catalyst (5 wt.%), and stirred magnetically at 400 rpm for 15 min at room temperature, respectively.

##### 3.1.2. Inorganic filler

Porous carbon adsorbent produced by the Blücher GmbH was chosen as dispersed filler phase. As a first step of preparation, carbon particles were dried in a vacuum oven at 100 mbar and 150°C for 12 hours to avoid any adsorbed components. The main characteristics of the chosen carbon filler is given in Table 1.

**Characteristics of carbon adsorbent**

Particle size distribution (>80%)	[ $\mu\text{m}$ ]	100–630
Average particle size	[ $\mu\text{m}$ ]	431
Average pore diameter	[ $\text{\AA}$ ]	18.68
Total pore volume	[ $\text{cm}^3/\text{g}$ ]	0.6357
Bulk density	[ $\text{g}/\text{l}$ ]	588

### 3.2. Methods

EDX technique was used for identifying the elemental composition of an area of interest. The EDX analysis system works as an integrated feature of a SEM. The output of an EDX analysis is an EDX spectrum. The EDX spectrum is a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element in the specimen.

In order to investigate pore blockage, two different types of EDX analysis were performed. Aim of the both analysis was to detect silicon (Si) and to observe PDMS penetration inwards the carbon particles. Herewith, EDX scan was carried out on the cross section area of single carbon particles. In the first analysis, EDX point-scan was applied to several predetermined depths from the surface through the center of a single carbon particle and Si presence was detected. A limited number of points on the cross section of the particle could have been examined with point-scan analysis. Secondly, for a detailed investigation of Si regions, an EDX line-scan analysis is performed along a line on the cross section area of the carbon particle. Line-scan profile with EDX technique plots the abundance of an element along a line. Since the line-scan analysis is conducted over more points, the counting statistics are much better. However, a drawback of the line-scan analysis is time limitation. SEM and EDX analysis were carried out by Zentraleinrichtung Elektronenmikroskopie (ZELMI), Technische Universität Berlin.

#### 3.2.1. Sample preparation for EDX scans

For EDX point-scan analysis, 4 different carbon samples were prepared. After drying, 1 g carbon was weighted into each of 4 glass jars and 2 of them were saturated with isooctane. Saturation was applied as follows: A mass of isooctane was added to the samples and they were stirred with a glass stirrer manually until isooctane was evaporated. Afterwards, all 4 carbon samples were mixed with prepared PDMS solution. For EDX line-scan analysis, another 3 carbon samples were prepared in the similar way, but all samples were saturated in isooctane. Amount of solvent and PDMS added to the point-scan (PS) and line-scan (LS) samples are given in Table 2.

Table 2

**Amount of solvent and PDMS mixed with point-scan (PS) and line-scan (LS) carbon samples**

Sample no	[-]	Saturated		Unsaturated		Saturated		
		PS-1	PS-2	PS-3	PS-4	LS-1	LS-2	LS-3
Mass of carbon	[g]	1	1	1	1	1	1	1
Mass of isooctane	[g]	3.5	3.5	–	–	5	5	5
Mass of PDMS solution	[g]	1.955	0.875	1.955	0.875	2.0	1.0	0.6

## 3.2.2. SEM and EDX analysis procedure

From each prepared sample, a single carbon particle was mounted on a specimen stub and cut into two halves with a blade manually in order to analyze cross section area of the particle. Specimens tend to charge when scanned by the electron beam, especially in secondary electron imaging mode. This causes scanning faults and other image artefacts. In order to avoid these effects, point-scan samples were investigated after sputter coating by gold and line-scan samples were investigated after sputter coating by carbon.

**4. Results and Discussion**

## 4.1. EDX Point-Scan Analysis

With two different amounts of PDMS addition, a total of 4 carbon samples were prepared, including 2 isooctane-saturated and 2 unsaturated samples (see Table 2). Figure 2 shows surface SEM pictures of these carbon particles. Surface of each sample was analyzed by EDX point-scan technique and Si was identified on the surface of all samples. It is obviously seen that there is a thick PDMS layer on the surface of saturated sample PS-1. This layer is not homogeneously distributed, even at some locations the layer is doubled depending on the high amount of Si in this sample.

In order to make a quantitative comparison, EDX analysis was applied on the cross section area of carbon particles. To investigate the degree of pore blockage that slows or blocks the diffusion of adsorbents into the pores, EDX point-scan analysis was applied to several depths in the carbon particles. The cross-sectional SEM pictures showing EDX point-scan analysis depths of samples are shown in Fig. 3.

Figure 4 shows the point-scan analysis of saturated carbon particle, PS-1; which has the higher amount of PDMS. EDX point-scan was carried out at five different depths: 5, 10, 15, 30, and 50  $\mu\text{m}$ . Si was detected at all of these depths. Indicated Si signal decreased from the depth 5  $\mu\text{m}$  to 50  $\mu\text{m}$  and no more Si was detected after 50  $\mu\text{m}$ . But, Si was detected up to 70  $\mu\text{m}$  depth of the unsaturated carbon particle, PS-3; which has the same amount of PDMS as PS-1 (Fig. 5). In both samples, Si signal decreased gradually from the surface towards the center of particles. The most important outcome was that PDMS penetration was deeper in the unsaturated particle than in the saturated particle.

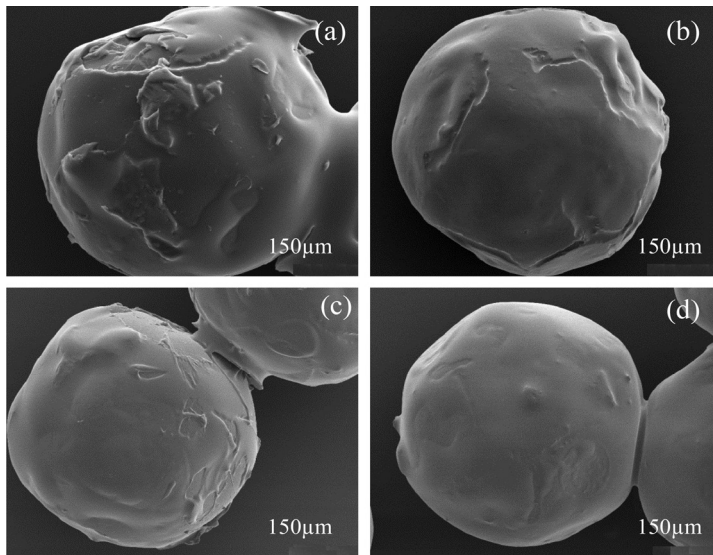


Fig. 2. Surface SEM pictures of saturated carbon particles: (a) PS-1, (b) PS-2; and unsaturated carbon particles: (c) PS-3, (d) PS-4

Rys. 2. Obrazy powierzchniowe SEM nasyconych cząsteczek węgla; (a) PS-1, (b) PS-2 oraz nienasyconych cząsteczek węgla; (c) PS-3, (d) PS-4

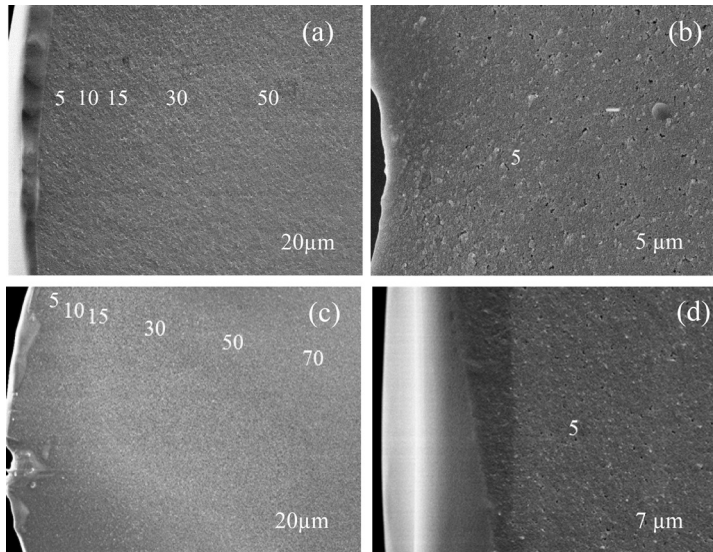


Fig. 3. Cross-sectional SEM pictures showing EDX point-scan depths of saturated carbon particles: (a) PS-1, (b) PS-2; and unsaturated carbon particles: (c) PS-3, (d) PS-4

Rys. 3. Obrazy przekrojowe SEM ukazujące punktowe głębokości skaningowe EDX nasyconych cząsteczek węgla; (a) PS-1, (b) PS-2 oraz nienasyconych cząsteczek węgla; (c) PS-3, (d) PS-4

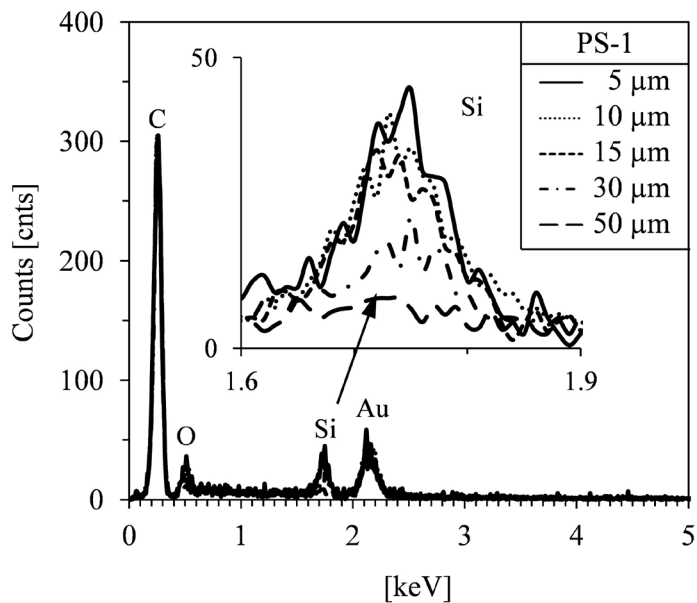


Fig. 4. EDX point-scan analysis of saturated carbon particle, PS-1

Rys. 4. Punktowa analiza skaningowa EDX nasyconej cząsteczki węgla, PS-1

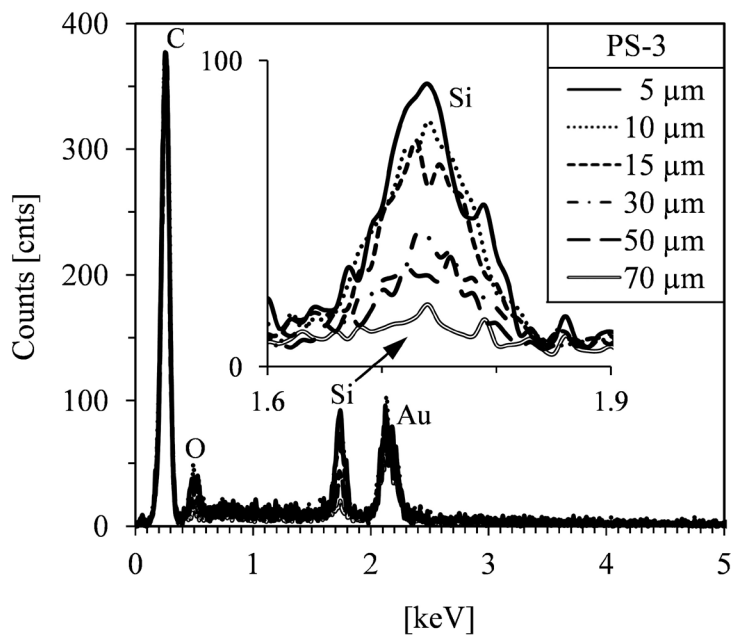


Fig. 5. EDX point-scan analysis of unsaturated carbon particle, PS-3

Rys. 5. Punktowa analiza skaningowa EDX nienasyconej cząsteczki węgla, PS-3

Saturated and unsaturated particles which include lower amount of PDMS were compared. EDX point-scan analysis of saturated particle PS-2 indicated no Si signal even in 5  $\mu\text{m}$  depth inside the particle (Fig. 6). But for the unsaturated particle PS-4, Si signal was detected at 5  $\mu\text{m}$ , but no more in the deeper pores (Fig. 7). Saturation process with isooctane showed an inverse relation to the pore blockage. This indicates an important advantage since PDMS can no longer enter the pores when pores are already saturated.

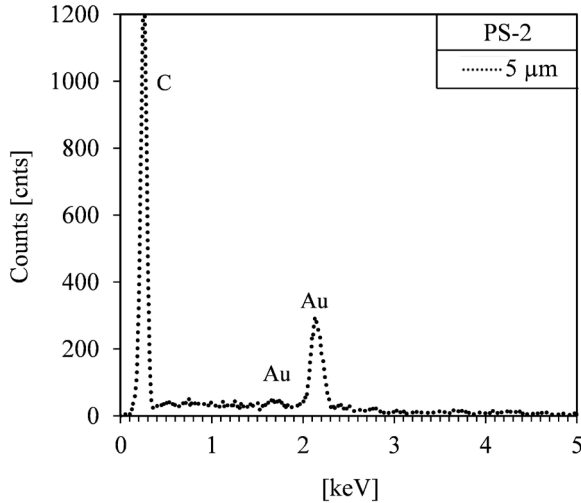


Fig. 6. EDX point-scan analysis of saturated carbon particle, PS-2

Rys. 6. Punktowa analiza skaningowa EDX nasyconej cząsteczki węgla, PS-2

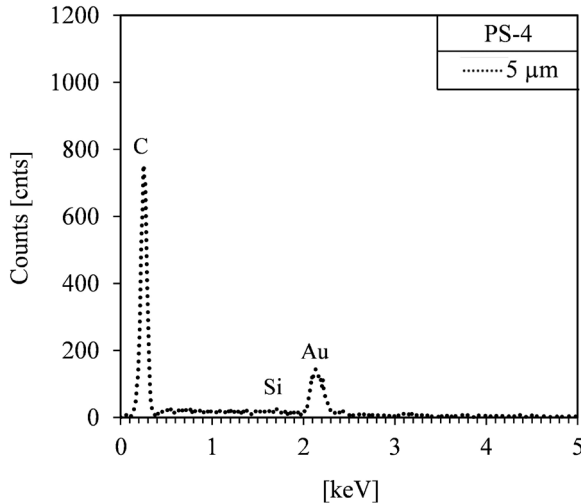


Fig. 7. EDX point-scan analysis of unsaturated carbon particle, PS-4

Rys. 7. Punktowa analiza skaningowa EDX nienasyconej cząsteczki węgla, PS-4



## 4.2. EDX line-scan analysis

It was observed by EDX point-scan analysis that polymer penetration is weaker in the isooctane-saturated carbon particles than in unsaturated particles. Therefore, another three isooctane-saturated carbon samples were tested with EDX line-scan analysis. The line-scan of EDX was applied to the cross-section area of saturated carbon particles at different PDMS additions in order to detect Si penetration profile along axial direction. Sample details are given in Table 2. For each sample, a total length of 155  $\mu\text{m}$  was scanned with a speed of 20 000 ms per each 5  $\mu\text{m}$  (32 points). Measurements were carried out at a voltage of 20 kV.

Figure 8 shows cross-sectional SEM pictures of line-scan applied saturated carbon particles and atomic percentage of total detected elements on the scanning line. Highest Si atomic percentage was detected in the first sample LS-1, which was mixed with highest amount of PDMS. Detected relative atomic percentage of Si showed a decline with the decrease of PDMS concentration. This was the expected result. But the most important point is that the degree of Si penetration also decreased.

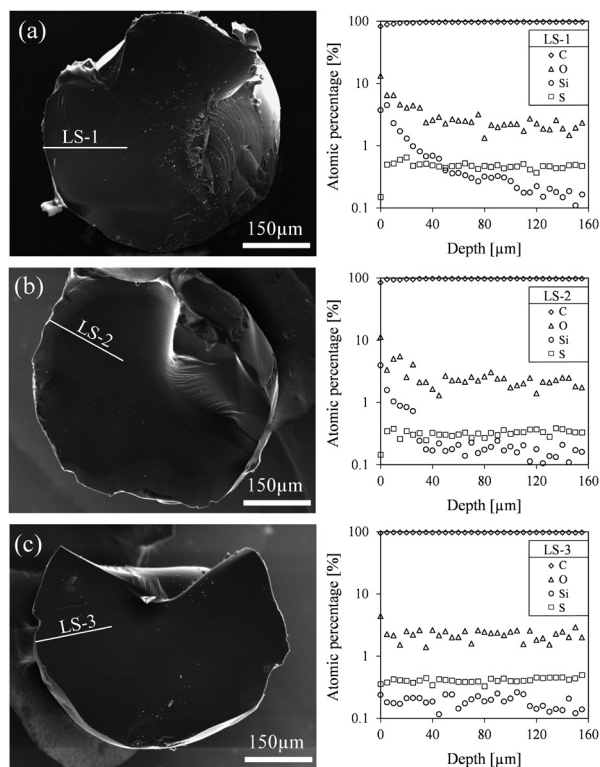


Fig. 8. Cross-sectional SEM pictures and atomic percentage of elements detected by EDX line-scan of saturated carbon particles: (a) LS-1, (b) LS-2, (c) LS-3

Rys. 8. Obrazy przekrojowe SEM oraz atomowy odsetek elementów wykrytych przez liniowy skaningu EDX nasyconych cząsteczek węgla; (a) LS-1, (b) LS-2, (c) LS-3

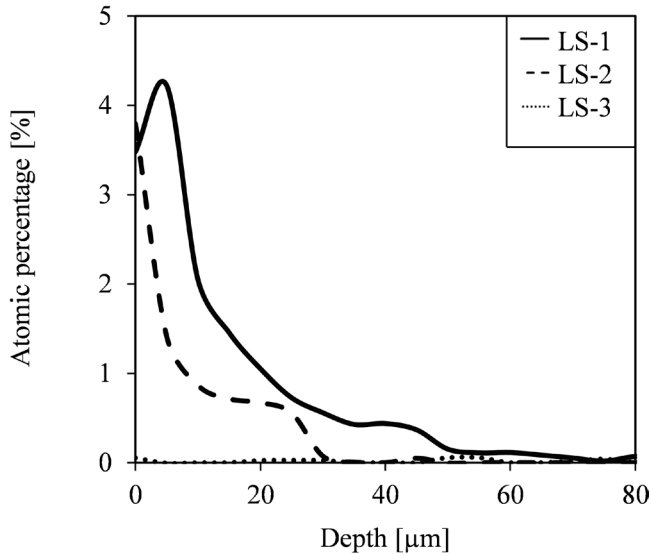


Fig. 9. Atomic percentage Si detected by EDX line-scan of saturated carbon particles: (a) LS-1, (b) LS-2, (c) LS-3

Rys. 9. Atomowy odsetek Si wykryty przez liniowy skaning EDX nasyconych cząsteczek węgla; (a) LS-1, (b) LS-2, (c) LS-3

Figure 9 shows decline of Si percentage of samples over the depth in detail. After approximately 50  $\mu\text{m}$ , no more Si was detected in the first sample LS-1. In the first 5  $\mu\text{m}$  depth of the first sample LS-1, it is clearly seen that there is a jump of Si percentage. This effect is simply due to the PDMS layer on the outer surface of the particle and it depends on the starting point of scan. Si percentage of the second sample LS-2, showed a sharp decrease at first 10  $\mu\text{m}$  and no more Si was detected after 30  $\mu\text{m}$ . Finally, no Si was detected in the third sample LS-3 with this analysis.

## 5. Conclusion

Pore blockage is a critical issue of MMM producing. Blockage does not allow gases to pass through the pores. Thus, pore blockage greatly decreases the selectivity and permeability. That causes polymer-particle interfacial defects and non-ideal morphologies in MMMs. It is necessary to add further pretreatment steps to the membrane formation procedure in order to avoid potential pore blockage.

In this contribution results showed that it is possible to reduce partial pore blockage via polymer chains with current strategy (pre-saturation process of activated carbon particles). PDMS penetrated easier through the pores of unsaturated carbon particle than saturated particle. Nevertheless, the impact of solvent saturation is still a topic of further investigations. Carbon particles which will be used in the MMM production have smaller particle sizes, approximately 10  $\mu\text{m}$ . For this reason, pore blockage must be reduced under 5  $\mu\text{m}$  intrusion depth.

Future work includes investigating of performance of different solvents and secondly, testing of permeation properties (permeability and selectivity) of produced membranes including a pre-saturation process.

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