The comparison of the three methods of specific surface evaluation - adsorptive porosimetry, inverse gas chromatography and mathematical method.

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Abstract. In the present study an attempt to determine the possibility of using novel measurement techniques for the evaluation of medical implants was made. The focus was put on the measurements of the specific surface area and associated characteristics of the knitted monofilament meshes made of polypropylene, used for the hernia treatment. As a part of examination, three methods of examination were compared - adsorptive porosimetry, inverse gas chromatography and mathematical method. The obtained results of the specific surface area confirmed the hypothesis stating that the results of specific surface area measurements depend on the applied measurement method.

1. Introduction
Hernias are serious health problems and if left untreated, can lead to severe complications and even death. One of the most common methods of treatment is the use of a polymer implant, which allows the "tension free" surgical operation [1,2]. Apart from the polymer used and its physical, chemical and mechanical properties, extremely important are structural parameters of the implant. Unfortunately, harmonized standards of Directive 93/42/EEC do not include this aspect in evaluation and also, at the stage of implants’ design standardized methods in this respect are not in use [3]. However, the ability of assessing surface properties would allow predicting the mechanism of action of the implant within the human body. It would also enable to create a more complete picture of the biomaterial properties and it could bring also the possibility to predict its mode of action in biological conditions.

2. Materials
In the frame of the presented work, two kinds of hernia meshes, commonly available on the market, were examined. The monofilament hernia meshes are made of polypropylene and are intended for medical use (implantable materials with over 30 days of use within the body). In the study, a warp knitted fabrics with two types of weave were examined. The raw material used in the manufacture of knitted fabric is polypropylene (PP), the structure of which is present in Figure 20. The density of the used PP was given by the manufacturer - 0,946g/cm³.

3. Methods
Basic structural characteristics, such as surface mass were tested in accordance with applicable standards – examination was performed in accordance with PN-EN 29073-1: 1994, on samples with an area of 10x10 cm. The surface mass determination was carried out in air-conditioned laboratory, at normal climatic conditions, that is T = 20°C, RH = 65%. The climatic conditions were in line with the requirements of PN-EN ISO 139: 2005. Thickness of the knitted fabrics was measured in accordance with PN-EN 5084:1999 standard. Fibres’ diameters were determined by pictorial method on the basis of SEM microscopy images. The average value was determined based on 20 measurements. Based on the surface mass and average thickness, apparent density was calculated according to the formula:
\[ \rho_p = \frac{m}{V} = \frac{S}{d} \]  

(1)

Where: \( \rho_p \) – apparent density, \( \text{kg/m}^3 \); \( m \) – mass of the sample, \( \text{g} \); \( V \) – sample volume, \( \text{m}^3 \); \( SM \) – surface mass, \( \text{g/m}^2 \); \( d \) – sample thickness, \( \text{mm} \)

The measurements were carried out using the apparatus - Porosimeter ASAP 2020 V3.01 H. The inverse gas chromatography was conducted by the use of Surface Energy Analyzer (SEA) produced by Surface Measurement Systems (SMS) Instruments. Examination of the surface morphology was carried out using high resolution scanning electron microscope NOVA Nanos 230 manufacturing company FEI equipped with an X-ray microanalyzer EDAX Apollo SDD.

4. Results

4.1. Structural properties

Surface mass was calculated as the mean of three measurements, thickness was tested fivefold. Number of measurements stemmed from the provisions in the standards. Mean diameters of monofilaments were calculated on the basis of 20 measurements. Numerical results are shown in Table 1, 2 and 3.

**Table 1.** Summary of surface masses measurements of the investigated samples

| Surface mass g/m² | Standard deviation u | u₀ a | u₀ c |
|-------------------|---------------------|------|------|
| Sample I 47,5     | 0,98                | 0,31 | 0,0000103 0,31 |
| Sample II 32,5    | 0,68                | 0,21 | 0,0000103 0,21 |

a Value given by Accredited Laboratory Lab Tex, where measurement were taken.

**Table 2.** A summary of thicknesses of the investigated samples

| Thickness mm | Standard deviation u | u₀ a | u₀ c |
|--------------|---------------------|------|------|
| Sample I 1,09| 0,05                | 0,02 | 0,0000103 0,02 |
| Sample II 1,22| 0,05               | 0,05 | 0,0000103 0,05 |

a Value given by Accredited Laboratory Lab Tex, where measurement were taken.

**Table 3.** A summary of fibres’ diameter of the investigated samples

| Diameter μm | Standard deviation u | u₀ a | u₀ c |
|------------|---------------------|------|------|
| Sample I 94,953| 0,054037024 2,07 | 0,0000103 2,07 |
| Sample II 85,6515| 0,054037024 1,19 | 0,0000103 1,19 |

a Value given by Accredited Laboratory Lab Tex, where measurement were taken.

4.2. Surface morphology

Surface morphologies of the investigated samples are presented in Figure 1 and 2. The monofilament fibres are circular, which allows using the pictorial methods for measuring its diameter. SEM micrographs presents fibres in the place of the node creation (a, b) and also the method measuring the diameter (c).
4.3. Specific surface area

The specific surface area was determined by three different methods - adsorptive porosimetry, inverse gas chromatography and mathematical method. The value of the specific surface area and derivative magnitudes measured by adsorptive porosimetry is presented in Table 4.

|                         | Sample I | Sample II |
|-------------------------|----------|-----------|
| **Surface area**        | BET      | m²/g      | 100.16 | 87.60 |
|                         | Langmuir | m²/g      | 3483.07 | 2151.51 |
| **Pore Volume**         | Single point adsorption | cm³/g | 0.0836 | 0.0737 |
|                         | Total pore volume of pores | cm³/g | | |
|                         | BJH      | cm³/g     | 0.0780 | 0.0688 |
| **Pore Size**           | Adsorption cumulative volume of pores | cm³/g | | |
|                         | (4V/A by BET): | Å | 33,4028 | 33,6608 |
|                         | BJH Adsorption average pore diameter | Å | 44,4650 | 44,4260 |
| **Horvath - Kawazoe**   | Maximum pore volume at P/Po = 0.005060074 | cm³/g | 0.000435 | 0.000382 |
|                         | Median pore width | Å | 8.495 | 8.504 |

Specific surface area and derivative magnitudes can be measured also by inverse gas chromatography (IGC). Examination of BET specific surface areas was conducted using IGC with the test gas - vapors of octane. Changes were observed by retention time and on this basis BET specific surface area was specified. The analysis was performed by defining center mass of the peak. Free surface energy was analyzed using the Schultz’s theory. The free energy of the dispersion component and the value of free energy for each of the gases used were determined. By measuring the retention
time of the pairs of respective solvents $K_a$ - acidic and $K_b$ - alkaline constant were determined. The numerical values of BET surface areas, the values of free energy for each of the gases used and acidic and alkaline constant are summarized in Table 5.

**Table 5.** Results of measurement of BET specific surface area by IGC

| Sample | Surface area | Free surface energy | Acid/alkaline properties | Dispersive surface energy |
|--------|--------------|---------------------|--------------------------|---------------------------|
|        | m²/g | Dichloromethane | Ethyl acetate | Ethanol | Acetone | Acetonitrile | 1 – Propanol | mJ/m² | Acid constant - $K_a$ | Base constant - $K_b$ | Acidity-Basicity Ratio |
| Sample I | 17.13 | 19.32 | 17.98 | 13.15 | 16.64 | 25.67 | 10.61 | 249.68 | 0.19 | 0.44 | 0.44 |
| Sample II | 9.28 | 11.36 | 5.99 | 3.61 | 6.00 | 3.00 | 8.10 | 27.33 | 0.05 | 0.22 | 0.24 |

Calculation of $S_{SA}$ by mathematical method was performed on the basis of the equations indicated in previous subchapter - IV.2.e:

$$S_S = l \cdot 2\pi$$  

(2)

The calculation of the length of the monofilament was performed based on the equation 23 indicated in subchapter - IV.2.e.

$$l = \frac{\rho gD}{\pi r^2}$$  

(3)

and recounted for 1 g of the product. The results of the above calculations are summarized in Table 6.

**Table 6.** A summary of results obtained by the use mathematical method

| Sample | $\rho_f$ | g | D | r | l | $S_S$ |
|--------|---------|---|---|---|---|------|
| Sample I | 43.578 | 1.09 | 10³ | 946 | 7091,012 | 2.114 |
| Sample II | 26.639 | 1.22 | 10³ | 42,826 | 5962,668 | 1.604 |

The comparison of specific surface area measurements made by three different methods is presented in Table 7 and Figure 3.

**Table 7.** A summary of results obtained by the use mathematical method

| Sample | Surface mass | Thickness | Apparent density | BET Adsorptive porosimetry | BET Inverse gas chromatography | Mathematical method |
|--------|--------------|-----------|------------------|-----------------------------|-------------------------------|--------------------|
| Sample I | 47.5 | 1.09 | 43.578 | 100.16 | 17.13 | 2.114 |
| Sample II | 32.5 | 1.22 | 26.639 | 87.60 | 9.28 | 1.604 |
5. Discussion

Based on the examinations carried out, it was demonstrated that each of the methods used resulted in obtaining different results. This is particularly due to the following:

5.1. Analytical methods

The applied two analytical methods are performed with the use of different test gases. In particular, for adsorptive porosimetry, a nitrogen gas is used, which is characterized by small size of the molecules and is an inert gas. The dimension of the molecule seems to have a crucial meaning during the measurement, as depending on this the tested gas molecules are able or are unable to settle on the analyzed surface and in pores of the specific dimension, and particularly on the basis of the number of settled molecules, the specific surface area is measured. In case of inverse gas chromatography, the tested gas used is octane, which has significantly bigger molecules, and what is also important, it can interact with the examined surface, which might disturb the measurement. The bigger size of the molecule makes it impossible to the tested gas particles to penetrate into the smallest spaces (pores) in the examined material. The result of this research confirmed, that in case of using bigger size of the molecule (IGC - octane), the results of the obtained BET surface were five to even ten times smaller, than in case of nitrogen molecule (Table 7). Moreover, a tendency was observed in which the results of Sample II measurements of specific surface area were lower than in case of Sample I for every method used. Performed studies have shown that there is a correlation between the sizes of particles deposited into the surface area of the tested material and the results of the specific surface area measurements. Taking into account the microporous structure of the product, it can be assumed that by the use of greater octane molecule in the examination, only the largest micropores will be taken into account. This will translate into decrease in the value of specific surface area. From the point of view of practice, surface modification or assessment of the interaction between the material and a living organism, the assessment by the IGC may more reflect the reality, because in all cases the size of the specific surface area will depend on the size of the biological elements to interact with, which usually have larger sizes than molecule of nitrogen. Therefore, from the practical point of view, e.g. the measurements of actual contact surface, the use of large molecules is thus legitimated, but from the point of view of identification of the material and its characteristics, the use of small particles measured by the specific surface area is more reasonable.
5.2. Mathematical method

This method is the simplest, but unfortunately with its application are associated major restrictions on the form of monofilament creating a range of textiles products for the use as an implant. These limitations are caused by the fact that the shape of the fibre is approximated by a cylinder and also it is assumed that porosity and roughness of the elementary fibre does not occur. In addition, it is assumed that the cross-sectional fibres’ shape is ideally oval, which in practice may vary considerably. Apart from this, the most frequently, a fibre creates a twisted yarn, then taking the cylinder as an alternate shape causes the significant omission of information for example on the different spaces between the filaments. As a result of the application of this method, the calculated specific surface area of the monofilament knitted fabric is burdened with a large error. The mathematical method due to the numerous limitations on the geometry of the monofilament, turned out the be not so much reliable, because is associated with committing a very serious error in the calculations, if there is no measuring the true density of the polymer, and the only assumption is based on the characteristics provided by the manufacturer. In this way, it was possible to obtain the deviation of more than 10%.

Adsorptive porosimetry examination involving the pore size distribution revealed that in the case of the tested materials, there exists a small level of porosity of the monofilaments. The identified pore size are classified into the group of micropores. Therefore, one should be aware that the requirement for the lack of porosity in the material is not completely satisfied. The presence of micropores is detected by adsorption techniques, however it is completely negligible in the mathematical method, which is based on calculations.

6. Conclusions

The obtained results of the specific surface area confirm that the differences between the results derive from the specificity of the measurement. In the case of analytical methods (adsorptive porosimetry and inverse gas chromatography), the main difference lies in the selected gas for analysis - namely the type and size of the gas molecules used for measurements, which determines the amount of particles deposited on the test surface, which then has an impact on the calculation of specific surface area.

Both of the selected analytical methods are suitable for evaluation not only specific surface area, but also associated characteristics like free surface energy of the sample, acid/base properties, pore size, pore volumes and etc. Apart from the physical, chemical and mechanical properties of the implant, extremely important are structural and surface parameters. The ability to determine these parameters would allow predicting the mechanism of action of the implant within the human body. Application of these measurement methods in the design of the implant will contribute to shaping the structural properties of implants/medical devices for their final application, as well as shaping their biological characteristics (which are heavily influenced by surface properties). These methods should be incorporated in the design stage of medical devices, as their results are a perfect complement to other methods of evaluation, thereby allowing to a fuller extent determine the expected properties and actions of the implant in a natural environment.

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