Measurement of the distribution of polyoxymethylene particle size using the laser diffraction method

Karol Prałat a, *, Małgorzata Łukasiewicz b, Piotr Miczko b and Katarzyna Lesiecka b

a Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry, Łukasiewicz’a 17 Street, 09-402 Płock, Poland
b Higher Vocational State School of President Stanislaw Wojciechowski, Polytechnic Faculty, ul. Poznanska 201-205, 62-800 Kalisz, Poland

KEYWORDS
Laser diffraction
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Particle size distribution
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ABSTRACT
The paper contains the results of experimental studies determining the size of grains of ground polymer (polyoxymethylene - POM). In the measurements a modern laser diffraction method was used to measure particle diameters. During the experiment, three series of measurements were carried out. Due to its properties, POM can be used as an additive to concrete and gypsum composites, increasing their strength. However, it is necessary to know the size of the polymer grains used. The grain size of building material additives is one of the many aspects that also directly influence the bonding time of composites and therefore determine their usefulness in the building industry. The paper presents an innovative method used in the control of many technological processes, which determines the usefulness of fine-grained fillers for building materials on the basis of their granulation results.

Introduction
The phenomenon of laser diffraction used in laser particle size measurement is widely used in research and development to control the quality of powdered products, contaminants, soil samples, technological processes in various industries: pharmaceutical, construction, chemical, food, metallurgy, etc. Particle size characterizes a given product, determines its strength and stability, which are very valuable in the control of the production process. [1–3]. Knowledge of the grain size of building materials and the micro-additives used is very important because it is one of many aspects that directly influence the speed of the bonding process and therefore determines the suitability of a product for the construction industry. The faster process of bonding building plaster, cement or adhesives takes place when the material

* Corresponding author: Karol.Pralat@pw.edu.pl (K. Prałat)
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is characterised by a high fragmentation of the binder, i.e. a fine grain size. Furthermore, the knowledge of particle size distribution (PSD) values of many materials is very important both in engineering practice and experimental research.

There are studies concerning particle size distribution in raw materials and different physical, chemical and mechanical properties of cement and plaster mortars. In articles [4–7] the effect of cement PSD on the kinetics of hydration and concrete strength was demonstrated. The influence of admixtures (slag and fly ash) on its properties was also evaluated [8–13]. The influence of particle size and shape in individual particles on the properties of hardened mortar was also investigated. [14,15].

Many research projects have developed and evaluated alternative methods for measuring the size of soil particles with gypsum, which include gypsum particle size distribution. Common laboratory methods for determining the size distribution of soil particles, including those containing large amounts of gypsum, rely on the complete removal of gypsum and more soluble salts, as they interfere with the dispersion of samples and the formation of a stable suspension of clay [16–18]. With this approach, particle size measurements only reflect the size distribution of essentially insoluble, mainly silicate, minerals and do not reflect the size distribution of the entire soil, including gypsum. [17]. Authors [19–21] proposed a method for determining the size of soil particles with intact gypsum, which consists in the suspension of a sample in BaCl₂ solution.

This paper presents and analyses the grain size distribution distribution of polyoxymethylene (POM) samples, as a potential filler for cement and gypsum mortars, obtained by laser diffraction measurements.

**Basic theory**

In the work [3], the authors presented the basic assumptions of the Fraunhofer theory presented below. When a collimated laser beam with wavelength $\lambda$ is an incident on a single spherical particle, the light diffracted in the range of a small forward angle can be approximated by the Fraunhofer diffraction theory if the particle size parameter, $x$, satisfies $x \gg 1$ ($x = \pi d / \lambda$, $d$ is the diameter of the particles). According to the Babinet principle and Fraunhofer diffraction theory, the diffracted light is given by the Airy function, i.e.

$$I(\theta, x) = I_0 \frac{\pi^2 d^4}{16 F^2 \lambda^2} \left( \frac{2 J_1(x \sin \theta)}{x \sin \theta} \right)^2$$

(1)

where $I_0$ is the intensity of the incident light, $\theta$ is the diffraction angle, $J_1$ is the Bessel function of the first kind of order 1, $\lambda$ the wavelength of the incident light, and $F$ the focal length of the Fourier lens. In practice, $\sin \theta \approx \theta$ because $\theta$ is very small, therefore

$$I(\theta, x) = I_0 \frac{\pi^2 d^4}{16 F^2 \lambda^2} \left( \frac{2 J_1(x \theta)}{x \theta} \right)^2$$

(2)

For a suspension of spherical particles, if the concentration is low enough so that the optical thickness ($\tau$) of the sample meets the condition of single scattering, i.e. $\tau << 1$, Equation (2) can be integrated over the range of particle sizes to obtain the distribution of the diffraction intensity as shown in Equation (3) [22].
Here \( n(x) \) is the number distribution of particles, and \( k = \frac{2\pi}{\lambda} \) is the wave number, Equation (3) is a Fredholm integral equation of the first kind [3,23].

**Experimental set-up**

The diffractometric method is based on the phenomenon of optical diffraction. The theoretical basis of the diffractometric method is the description of the phenomenon of optical diffraction by means of Fraunhofer transform. The possibility of practical application of this description appeared only after the construction of the laser and the development of methods and devices for the analysis of optical images.

The optical system (Fig. 1) for the analysis of optical images consists of a monochromatic light source (laser), an optical system forming its beam, an optical image formed by a suspension of powder grains in a liquid allowing this light to pass through and causing it to diffract at grain boundaries, an optical transformation system that transforms the transmitted light beam, a beam image detector, a transducer and a computer recording data. The diffraction method is used in many industrial branches for granulometric evaluation of grains, e.g. in construction, food and pharmaceutical industries [12,13,24–27].

![Fig. 1 Laser granulometer](image)

The transformed image in the granulometer and its transformation are placed in the focal points of the lens. The deflection of the light wave occurs at the borders of permeable (liquid) and impermeable (powder grains) media, which generates the image in the form of a diffraction grid. The lens concentrates all the bent and passing rays of light, creating a diffractive image called a diffractogram in the form of light and dark stripes or spots. With the resulting image it is possible to calculate the dimensions of the distance between the grid stripes. To identify the diameter of the grains, it is necessary to measure the distance between the stripe and the optical axis as well as the brightness intensity of the stripe. The image obtained allows us to conclude that the greater the distance between the stripe and the optical axis, the smaller the size of the tested grains. In addition, the higher the brightness intensity of the stripe, the more grains of given dimensions are present in the entire test sample.

The Analysette 22 MicroTec Plus laser particle analyser from FRITSCH GmbH Milling and Sizing (Fig. 2) was used to measure the size of the grains, using the reverse Fourier system according to ISO 13320. This device is equipped with a green laser and an infrared laser. The instrument has a modular structure, which includes a measuring unit and appropriate sample preparation units: wet or dry. In the presented studies, the meter was used to analyse samples...
of material suspended in a liquid, in this case water. The larger unit is the measuring unit, while the smaller dispersing unit is the dispersing unit.

The sample was added to a dispersing unit, then pumped into a measuring cell containing two semiconductor lasers of different wavelength ranges. The green laser is used to detect smaller particles and the infrared laser to detect larger particles. The device is controlled by MaScontrol software, which allows the meter to be operated. It contains a list of ready-made standard operating procedures, including commands to fill the measuring cell with water, clean or complete the measurement. The tests are carried out in an automated manner, and the user is kept informed of each and every one of the following from the activities of the analyser.

![Fig. 2 Laser meter of size of particles Analysette 22 MicroTec applied in the research.](image)

In the device shown in Fig. 2, it is possible to measure grain diameter in the range from 0.08 μm to 2100 μm. The grain size measurement by means of a diffractometric method using a laser and a computer is very precise. The device does not require any calibration based on basic physical properties. With Fraunhofer's theory, there is no need for detailed knowledge of the physical properties of materials, such as density, and the total measurement time of the sample is 2-3 minutes [29,30]. During measurement, the flux absorption shall be within the range 10-15%, which indicates the optimal amount of the tested material added to the dispersing medium. A special photodiode, which is located in the test instrument, measures the intensity of an undispersed laser beam. This intensity is 100% when there is no sample in the cell. When a sample is placed in the device, part of the light is scattered, thus reducing the intensity of the light stream falling on the photodiode. The paper presents a study of grain diameter of ground polyoxymethylene by diffractometric method and an attempt to determine its usefulness as a filler for building materials.

**The polymer used in the test**

Polyoxymethylene (methylene polyoxide; POM) used in the study is an organic chemical compound from the group of polyethers used for the production of thermoplastic plastics (thermoplastics). This polymer is obtained by polymerization of formaldehyde.

POM is a very good construction material, used in all branches of industry. It is white as standard, but can be easily coloured in practically any colour in the process of preparing granules for injection or extrusion. It is a material used mainly for the manufacturing of products with high durability requirements, such as drive elements (rollers, shafts, gears, rods, etc.),
structural elements (bodies, handles), elements of water and gas fittings, sliding rings and bearing elements or elements of sealing units for high pressures. It is used in vehicles, household appliances, electronic office equipment as well as automation and control equipment. Table 1 summarizes the basic physical properties of the polyoxymethylene used in the study.

Table 1. Physical properties of polyoxymethylene applied in research.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1410</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Water absorption (23°C)</td>
<td>0.65</td>
<td>%</td>
</tr>
<tr>
<td>Humidity absorption (23°C/50%RH)</td>
<td>0.2</td>
<td>%</td>
</tr>
<tr>
<td>Melting temperature (10°C/min)</td>
<td>166</td>
<td>°C</td>
</tr>
<tr>
<td>Flammability</td>
<td>HB</td>
<td>Class</td>
</tr>
<tr>
<td>Tensile modulus (1mm/min)</td>
<td>2850</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile stress at yield (50 mm/min)</td>
<td>64</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile strain at yield (50 mm/min)</td>
<td>9</td>
<td>%</td>
</tr>
<tr>
<td>Nominal strain at break (50 mm/min)</td>
<td>30</td>
<td>%</td>
</tr>
<tr>
<td>Tensile creep modulus (1h)</td>
<td>2500</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile creep modulus (1000h)</td>
<td>1300</td>
<td>MPa</td>
</tr>
<tr>
<td>Charpy impact strength at 23°C</td>
<td>180</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Charpy impact strength at -30°C</td>
<td>160</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Charpy notched impact strength at 23°C</td>
<td>6.5</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Charpy notched impact strength at -30°C</td>
<td>6</td>
<td>kJ/m²</td>
</tr>
</tbody>
</table>

The obtained, milled polymer due to its large size fragments (Fig. 3) did not meet the conditions for granulometric measurement, which assumes diameters of measured particles smaller than 2 mm. Therefore, prior to the measurements, the granules were sieved through sieves with mesh sizes less than 2 mm. As a result, fractions (Fig. 4) were obtained, which made it possible to measure them using an analyser.

![Fig. 3 Polyoxymethylene constituents prior to the sieving process.](image-url)
Experimental results

The sample of ground polyoxymethylene (POM) was characterized by good wettability. Standard measurement parameters were used for the sample: 60% of the pump power and 100% of the ultrasonic and light power were used. The time of removing air bubbles from the liquid was 10 seconds, while the time of adding the polymer sample to the dispersing unit did not exceed 30 seconds.

Three measurements were taken for each polymer (Table 2), thanks to which it was possible to observe variability of the obtained results of measurements of diameters of particles dispersed in water. In all the samples the absorption range of 10-15% was obtained. The amount of the analysed sample needed for dispersion was therefore optimal.

It can be noticed (Fig. 5) that in the tested sample there are significant amounts of particles with diameters: 1 μm, 10 μm and 500 μm. There are practically no POM particles with diameters in the range of 20-300 μm. For the investigated polymer it was observed that during three consecutive measurements the number of particles with diameters ranging from 1 μm to 5 μm increased. The forces of interaction cause small particles to merge into larger clusters.
Table 2. Results of laser diffraction analyzes of building materials particle size distribution.

<table>
<thead>
<tr>
<th>Studied material</th>
<th>Particle diameter $d$ ($\mu$m)</th>
<th>Average particle size distribution $\phi_{ave}(d)$ (%)</th>
<th>Particle size distribution $\phi_1(d)$ (%)</th>
<th>Particle size distribution $\phi_2(d)$ (%)</th>
<th>Particle size distribution $\phi_3(d)$ (%)</th>
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<tr>
<td></td>
<td>0.4</td>
<td>4.5</td>
<td>5.0</td>
<td>4.0</td>
<td>4.5</td>
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<tr>
<td></td>
<td>0.5</td>
<td>6.7</td>
<td>10.0</td>
<td>5.0</td>
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<tr>
<td></td>
<td>0.6</td>
<td>15.0</td>
<td>25.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>29.2</td>
<td>42.6</td>
<td>25.2</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>44.9</td>
<td>50.0</td>
<td>49.9</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>52.4</td>
<td>50.6</td>
<td>56.8</td>
<td>49.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>60.3</td>
<td>50.7</td>
<td>64.1</td>
<td>66.2</td>
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<tr>
<td></td>
<td>6</td>
<td>60.9</td>
<td>52.4</td>
<td>64.1</td>
<td>66.2</td>
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<td>8</td>
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<td>58.1</td>
<td>66.3</td>
<td>68.4</td>
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<td></td>
<td>10</td>
<td>67.1</td>
<td>62.4</td>
<td>69.8</td>
<td>69.1</td>
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<tr>
<td></td>
<td>20</td>
<td>78.5</td>
<td>74.4</td>
<td>81.8</td>
<td>79.4</td>
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<tr>
<td></td>
<td>25</td>
<td>79.1</td>
<td>75.1</td>
<td>82.4</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>79.2</td>
<td>75.2</td>
<td>82.4</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
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<td>75.2</td>
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<td>75.2</td>
<td>82.4</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>79.2</td>
<td>75.2</td>
<td>82.4</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>80.3</td>
<td>76.5</td>
<td>83.3</td>
<td>81.1</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>90.1</td>
<td>88.3</td>
<td>91.6</td>
<td>90.5</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>99.0</td>
<td>98.8</td>
<td>99.1</td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 6 graphically presents the results of the study and characteristic statistical parameters such as: diameters of characteristic grains $d_{10}$, $d_{50}$, $d_{90}$, mode and span, where the last parameter is described by the equation (4):

$$\text{Span} = \frac{d_{90} - d_{10}}{d_{50}}$$

(4)
Fig. 6. Sizes of characteristic particles determined by means of laser diffraction method in samples of polyoxymethylene: a) 1\textsuperscript{st} measurement, b) 2\textsuperscript{nd} measurement, c) 3\textsuperscript{rd} measurement.

On the basis of diagrams (Figs. 6a-6c) it was found that in the investigated polymer there are harmful to health fractions of dust with diameters smaller than 2.5 µm, which may cause cancer. In the tested samples, dangerous particles constitute more than half of all grains. During the possible application of polymer in building composites it is important to pay attention to this fact, especially during its dosing into composite mixtures, when significant dusting of components may occur.

Diagram in Figure 7 presents the results of average particle size distribution approximation as a function of grain diameter of the tested polymer sample.
Fig. 7 Results of approximation of average particle size distribution of polyoxymethylene as a function of grain diameter.

For the powdery polymer material investigated in the experiment, a generalised relationship was proposed, described by equation (5):

\[
\phi_{ave}(d) = A \cdot \ln(d) + B
\]

where A and B are constant equations of values 6.80 and 50.1 respectively. The obtained high value of the parameter \( R^2 \) = 0.879 proves the good conformity of experimental results with the proposed mathematical relation.

**Conclusion**

- The laser diffraction method used in the research is characterized by short measurement time. Moreover, its additional advantage is high reliability and repeatability of results.
- It has been confirmed that laser granulometric analysis provides accurate information on the distribution of the size of polyoxymethylene grains in the range of hardly measurable fine grains (< 500 μm), giving also information on the distribution of grains up to 2000 μm.
- It was observed that in the tested sample there are significant amounts of particles in three large clusters, close to the diameters: 1 μm, 10 μm and 500 μm. Practically no POM particles with diameters ranging from 20 to 300 μm were observed.
- For the investigated polymer it was observed that during three consecutive measurements the number of particles with diameters ranging from 1 μm to 5 μm increased. This proves the formation of agglomerates of particles and their joining into larger clusters.
- The sample was characterized by very good wettability and did not require the use of an additional surfactant to reduce the surface tension at the contact between liquid and solid. In the case of these studies, water proved to be a suitable dispersion liquid.

It was found that in the studied polymeric material there are dust fractions with diameters smaller than 2.5 μm, harmful to health, which are retained in the human body in the lungs. For this reason, it is necessary to work very carefully with this polymer. However, due to its mechanical properties and hardness, POM can be considered as an additive to mortars, concrete and gypsum. However, additional testing is needed before the material can be used for this purpose.
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