Use of polystyrene production wastes in selective laser sintering processes

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Abstract. The purpose of this study is to determine the possibility of using polystyrene waste in Selective Laser Sintering (SLS) technology. The powder was subjected to mechanical and chemical influences and was studied in optical and IR microscopes. Test samples were obtained on the sPro 60HD unit (3D Systems, USA).

Introduction
The efficient use problem of natural resources is an urgent task for mankind. Therefore, reduction of production waste solves two problems: saving natural resources and increasing the producer's profit. In the production of polystyrene granules, a large-dispersed powder with a large spread of particle sizes and irregular geometry is obtained as a waste. From waste, it is possible to obtain low-grade products, such as disposable tableware, industrial containers, Petri dishes, etc. Producers are interested in developing new methods of processing for the use of waste in the production of high-quality products.

Additive technologies are one of the modern production methods, where creation of a physical model occurs layer by layer in the CAD model. In technologies such as SLS, SLM, 3DP, powder compositions are used to create models. One of the most popular technologies is selective laser sintering (SLS). In this technology, a polymer or composite powder, sintered by an infrared CO₂ laser with a wavelength of 10.6 μm, is used to create models. In installations of Selective Laser Sintering, a uniform powder with dispersion up to 90 μm with good rheological properties is used. In comparison with other methods of additive production, SLS is highly versatile in terms of the consumables choice. This includes various polymers (polyamide 2200, polyamide 11, polyetheretherketone, polymethyl methacrylate, polycaprolactone, polystyrene [1,2,3], polymeric compositions with metal alloys (steel, titanium, precious metals, cobalt-chromium alloys) and sand mixtures. However, 95% of the powder used in the SLS technology is occupied by polyamide 12. The production uses high-quality and pure raw materials, which leads to a high cost of SLS-powder.

If analogy with standard foundry technologies for the production of polymer products is used, the use of polystyrene is more widespread. It is also known to use polystyrene in the SLS process to create
models used in casting for shell molds [5,6,7]. Therefore, a goal of the work is to investigate the possibility of using the polystyrene production waste in Selective Laser Sintering processes.

Main part

Pesticides from Nizhnekamskneftekhim, the Republic of Tatarstan, Russia, were used as feedstock. Using the optical microscope Premiere WF 10X DIN18mm, the geometry of the particles was studied and their size was determined. The dispersion composition was determined by screening through sieves with different mesh sizes at the Vibrogroot GV30 installation. Figure 1 shows photographs of the raw material obtained by an optical microscope. Particles have a large dispersion in size, as well as an irregular geometric shape. Particles measuring from 350 μm to 500 μm were observed. Figure 2 shows the histogram of the particle distribution.

![Figure 1 - Polystyrene starting powder under a microscope.](image1.jpg)

![Figure 2 - Disperse composition of the powder.](image2.jpg)

It was found that the starting powder consist particles with a size from 120 μm to 300 μm. There are also large particles from 300 μm (about 36%).

To determine the fluidity, a glass funnel was used with an glass funnel diameter of 7 mm. A certain amount of material was poured into the funnel, the hole was opened and the time of the material expiration was measured. The original powder did not spill out of the funnel, which indicates its poor flowability, the presence of large particles and their irregular geometry.

To determine the elemental composition of the powder, a PerkinElmer Spotlight 400 infrared microscope was used. An IR imaging system with a fast scanning interferometer, a matrix detector, an ATR probe, and an ATR image system. Simultaneous operation in the IR and visible ranges.
Modes of operation: transmission, reflection, micro-ATR, ATR image. The spectral range is 7800 - 600 cm\(^{-1}\) (scanning at a point); 7800 - 720 cm\(^{-1}\) (image mode). The geometric accuracy of the resulting image is ± 0.0013%, linearity> 99%. The signal / noise ratio is better than 50000: 1 (point scan), 800: 1 (image mode). The pixel size is 50, 25, 6.25 and 1.56 microns. Scanning time is 1.6 s. The rate of accumulation of spectra is 170 spectra of the full range in min.

![IR spectrum images](image1)

Figure 3 - a) IR spectrum of the initial polystyrene powder of PAO "Nizhnekamskneftekhim", b) IR spectrum of the powder after grinding in a vibratory mill, c) IR spectrum of the powder after grinding on a disintegrator, d) IR spectrum of the powder after treatment with a chemical solution.

There are no foreign polymers in the powder, which indicates the qualitative composition of the raw materials, which does not require additional chemical purification. Therefore, it was decided to sinter raw materials, and if necessary, increase the rheological properties. Powder materials used in SLS technology must meet certain characteristics in terms of dispersion, particle shape and surface state, namely: dispersion - 20-90 μm, the shape of the particles must be spherical (for good flow of the powder, the material will not be strongly compacted by the roller ), the surface must be hydrophobic.

In experiments on selective laser sintering, we used the sPro 60 HD (3D Systems), USA. sPro 60 HD is an industrial selective laser sintering plant that creates physical models from powder compositions, mostly polymer ones. This installation is actively used in aircraft building, machine building, automotive industry, military-industrial complex, medicine for creating prototype models. Features: the construction area is 381x330x437 mm, the thickness of the layer is 0.08-0.15 mm, the printing speed is 1.0 l / h, the scanning system is ProScan CX (digital), the scanning speed is 6 m / s, the laser power is - 70 W / CO\(_2\) laser. The installation uses commercial materials - polyamide, polystyrene, polypropylene, glass-filled nylon 12.
It is known that the glass-transition temperature of the material is $T_g = 89 \degree C$. Do not exceed this temperature on the surface of the layer to avoid sticking the material to the screed roller. The layer thickness is 150 $\mu m$. A laser power of 28 W is required for a layer of 150 $\mu m$. Laser scanning speed - 6 m/s.

To improve the rheological properties, several methods of physical action have been applied: grinding in a vibratory mill, grinding in a disintegrator, chemical action to reduce the coagulation process. Vibrating mills are designed for finely grinding brittle powder materials due to the impact and abrading action of milling bodies, which are located together with the grinding material in a vibrating drum. As grinding bodies, we took ceramic balls of diameters with an average of 1 cm, which fill the volume of the mill by 80%. The vibrating mill drum is driven into oscillatory motion by means of a rotating shaft with unbalance. The vibration frequency was 25 times per second, amplitude 4-5 mm.

The original powder was ground in a vibrating mill for 2 hours. The dispersion composition of the obtained powder is shown in Figure 2. Flowability - 5 grams of powder precipitated from the glass funnel in 5.8 seconds. Analysis on an IR microscope showed no change in the chemical composition. The IR spectrum is shown in Fig. 3b.

In the experiments, the disintegrator DZG-200T-20L was used. The disintegrator consists of two rotating rotors in opposite directions, which are mounted on separate shafts and encased in a casing. On the rotor disks, concentric circles have 2 to 4 rows of circular cylindrical fingers, so that each row of one rotor freely enters between the two rows of the other. The material for crushing is fed to the central part of the rotor and, moving to the periphery, is subjected to repeated impacts of the fingers, which rotate in opposite directions. Technical characteristics of the disintegrator: productivity - $10 \div 50$ kg / h, the number of rotors - 2 pcs, rotational speed - 2800 rpm.

As can be seen from the diagram in Fig. 2, particles with a size of 400-500 $\mu m$ were milled and moved to the region of 40-300 $\mu m$. Flowability of the powder improved - from the glass funnel 5 grams of powder poured out in 5.5 seconds.

Figure 4 shows a snapshot of the powder after grinding on a disintegrator under a microscope with a 20x magnification. Powder particles larger than 300 $\mu m$ were not detected.

The treatment with surfactants was carried out in a chemical reactor at room temperature. The surfactant solution was mixed with the powder in a ratio of 1:10 and was periodically mixed for 5 hours. The powder was Figure 4 then filtered off, washed with water and dried at a temperature of 600 $\degree C$. Surfactant treatment was carried out in order to reduce the attraction of particles and increase the fluidity of the powder.

As seen from the IR spectrum, the chemical composition does not remain on the surface of the powder. The precipitation of 5 grams of powder from the glass funnel took place for 12 seconds.
Thus, a negative result is observed, a decrease in fluidity occurs. The dispersion composition didn’t change.

Figure 5 - Sample powder under a microscope (20x magnification)

Carrying out the experiment from the initial polystyrene powder in the Selective Laser Sintering unit sPro 60 HD. Due to the low bulk density and the large particle size, the powder does not cover the entire construction area. This leads to the formation of pits in the central zone of construction (Figure 6a).

Figure 6 - The sintering process of the powder in the sPro 60HD unit: a) the starting powder; b) powder after the vibrating mill; c) powder after the disintegrator; d) powder treated with surfactant.

Figure 7 - The obtained test samples: a) from the original powder; b) from the powder after the vibrating mill; c) from the powder after the disintegrator; d) from a powder treated with a surfactant.
Figure 8 - Obtained test samples under a microscope with a 20x magnification: a) from the original powder; b) after the vibrating mill; c) after the disintegrator; d) after treatment with surfactant.

Figure 7 shows the appearance of the sample. The sample was of low strength and crumbled in the hands. The weight of the test sample was 0.58 g, density - 0.21 g / cm3. It consists of hotel blocks measuring 600-700 microns in size. Between the blocks, voids from 50 μm to 200 μm were formed. This caused high fragility and porosity.

Selective laser sintering of polystyrene powder after grinding on a vibrating mill made it possible to obtain stronger products. When the samples were examined under a microscope, it was found that the samples became more dense, the contours were clear. The weight of the test sample was 0.81 g, density - 0.29 g / cm3.

Carrying out the experiment from polystyrene powder after grinding on the disintegrator. The weight of the test sample was 0.95 g, the density became 0.34 g / cm3. As can be seen in Figures 7c and 8c, the contours of the sample become more distinct. The voids decreased to 200-400 microns.

Carrying out the experiment from polystyrene powder after surfactant treatment. The sample weight was 0.94 g. The density of the samples did not change. Treatment of the powder with surfactant solution is effective only when the particle size is less than 30 μm.

**Conclusion**

It is necessary to find a method for reducing the particle sizes below 100 μm and giving a spherical shape.

As a result of the research it was found out that the best way for mechanical grinding of the powder is the disintegrator. But the dispersion is not enough to use the powder in selective laser sintering. To obtain the necessary dispersion, cryogenic grinding should be used [4].

For good flowability, it is necessary to achieve the sphericity of the powder particles. To obtain spherical particles, an experiment with plasma spheroidization is needed.

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