The microstructure study of CJP products

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Abstract. The aim of work is research the microstructure of the products obtained in the ProJet
160 by ColorJet Printing technology. An IR spectrometer and a scanning electron microscope
were used to analyze the structure. Analysis of IR spectra showed that when the gluing
component was added, redistribution of the intensities of the absorption bands in the 3600–
3500 cm⁻¹ and 1130–1080 cm⁻¹ region and the appearance of new lanes in the 3403 cm⁻¹ and
1685 cm⁻¹ region were observed. This indicates the phase transformation of the gypsum
component under the action of water.

Introduction.

The technology of additive manufacturing is widely used in the manufacture of unique
and single products. One such technology is ColorJet Printing (CJP) [1]. The resulting
products consist of gypsum and polymer, while they have a porous structure. Their further
impregnation with epoxy resins makes it possible to use these products as models used for
casting molds. Epoxy resins provide the necessary strength and have a high durability in
comparison with wooden models. This is especially important in the manufacture of
magnesite forms, since stronger loads are observed when compacting [2,3,4,5,6,7,8].

Powder material with a roller is applied to the surface of the platform. The print head
sprays the binding fluid onto the surface of the applied powder layer. The drop-on-demand
method, developed by Hewlett-Packard, uses the same method as the gas bubble method to
deliver ink from the powder reservoir to the heating element. However, in the drop-on-
demand method, a special mechanism is additionally applied for the ink supply, while in the
gas bubble method this function is assigned exclusively to the heating element. A special
mechanism is implemented on the basis of the following physical phenomena. As a rule, the
surface tension acts on the particles of the liquid phase to maintain the sphericity of the
charged particles of the ink. The surface tension is reduced, which leads to the fission of the
particle into smaller parts. This property of the particles to be split is used to produce foggy
ink particles that flow to the nozzle outlets controlled by electrical signals. The heating of the
ink under this method occurs up to 650 °C, as a result, all the ink passes into the gaseous state
and the color shift occurs at the molecular level. The drop-on-demand technology ensures the
fastest ink application, which significantly improves the quality and speed of printing. The
color representation of the image in this case is more contrast. In this technology, the management of ink particles is performed with a constant deflecting field due to the regulation of their electric charge. Therefore, each particle emitted from the nozzle receives its "own" information in the form of a different value of the electric charge, which ensures the printing of high speed and print quality.

After application of the binder, the construction platform is lowered by 150 μm and the printing algorithm is repeated layer by layer. The internal structure of the products is interesting. CJP includes two main components: core and binder. In this case, we can observe a difference in the sprayed doses on the perimeter and core. Therefore, the aim of the work was to study the structure of used powders and obtained products, determination of the binder component influence on the resulting microstructure.

**Experimental part:**

3D Systems ProJet 160 is a professional 3D printer company 3D Systems, USA. Has become widespread in the field of prototyping for visualization of engineering tasks, design and architecture. The printer's working chamber has a build area of $236 \times 185 \times 127$ mm. The working chamber contains: a cartridge with a reinforcing liquid, a filter, a vacuum pump, a printing head moving system in a horizontal plane, a platform, a box for assembling the powder with a frontal overflow.

As the printhead in the fast axis node, the HP 11 cartridge is used. This cartridge is attached to the carriage as shown in Figure 1.

![Figure 1 - The carriage and print head assembly. The image is taken from the source [1].](image)

To start the work of manufacturing the desired product, you need to import a file with a 3D model (possible formats: 3DS, .BLD, .FBX, .PLY, .STL, .SFX, .VRML, .ZBD, .ZCP, .ZPR) into special software 3DPrint. Then the model divides into the thinnest horizontal layers. ProJet 160 prints layers of thickness of 0.15 mm. Data that displays information about these layers is loaded into the printer. Further all the work is done by the ProJet 160 itself.

The principle of work consists in layer-by-layer creation of the model. The minimum topological dimension of one element of the model in the X and Y axes is 0.4 mm. The model creation area is filled with the first layer of powder, then the print head applies a special adhesive to the areas where the layer of the future model is located. After that, the second, third, and all other layers transmitted by the software to the printer are filled in the same way.
In the printing process, the non-glued powder remaining around the product serves as a support function so that it is possible to create complex and structurally fragile models. Also, if you put several models for simultaneous processing, the powder will ensure the safety of each model. After printing, the product needs time to allow the adhesive to completely grasp the powder. Usually it takes 1-2 hours. Sometimes more than 2 hours, depending on the size and number of objects. During the extraction of the part from the powder, it is recommended to use special nozzles in order to not damage the fragile parts of the product.

After that it is necessary to further strengthen the product. For this, a fixer is used. Fixer is a special compound that strengthens the surface of the product. There are a number of fixers, but their strength indicators differ from each other.

![Graph of flexural strength using different types of fixers.](image)

Figure 2 - Graph of flexural strength using different types of fixers. [2]

To verify the print quality of the printer, the structure and composition of the powder and the product are examined after printing. For this, X-ray scanning and IR spectroscopy are performed, respectively. SEM images of the powder were also made using an electron microscope, shown in Fig. 3.

![SEM image of powder.](image)

Figure 3 - SEM image of powder.
A detailed analysis of the powder showed the presence of particles of two types, to refine the composition of the powder, the elemental composition was examined using a scanning electron microscope. The results of the studies are shown in Figure 4. It was shown that the powder particles having a dark shade on the SEM image mainly consist of carbon and oxygen, which may indicate their organic origin.

Principle of IR spectroscopy: infrared radiation passes through sample. There is excitation of vibrational motions of molecules or their separate fragments. In this case, the intensity of light passing through the sample is weakened. However, absorption doesn't occur in the entire spectrum of the incident radiation, but only at those wavelengths whose energy corresponds to the excitation energies of vibrations in molecules under study. Consequently, wavelengths (or frequencies) at which the maximum IR radiation absorption is observed can indicate the presence of certain functional groups and other fragments in the sample molecules.

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 4.79     | 8.17     |
| O K     | 52.88    | 67.69    |
| S K     | 19.66    | 12.56    |
| Ca K    | 22.66    | 11.58    |
| Total   | 100.00   |          |

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 47.13    | 60.67    |
| O K     | 30.97    | 29.93    |
| S K     | 9.96     | 4.80     |
| Ca K    | 11.93    | 4.60     |
| Total   | 100.00   |          |

Figure 4 - Elemental composition of powder particles.

As a IR spectroscopy result of a sample of the VisiJet PXL Core composite material and the details printed from the same material with the addition of a fixing liquid, the following spectra were obtained.
IR spectroscopy of the reinforcing liquid was also performed, as shown in Figure 6. After analyzing the data, we came to the conclusion that the VisiJet PXL core composite material is a mineral of the sulfate class, in terms of calcium sulfate hydrate (CaSO₄ · 2H₂O). The absorption lines in the IR spectrum of the composite can be attributed to the 3600-3500 cm⁻¹ and 1618 cm⁻¹ region to the crystallization water [4], which is part of the gypsum molecule, the bands in the region of 1130-1080 cm⁻¹ and 880-596 cm⁻¹ to SO₄ anions. [3]

Weak lines in the range 3000-2800 cm⁻¹ can be attributed to the groups CH₂ and CH₃ of linear polymer chains, in the range of 1600-1500 cm⁻¹, to nitro groups (NH), or to benzene rings. [4]

When analyzing the infrared spectra of a component, a redistribution of the intensities of the absorption lines in the 3500-3600 cm⁻¹ and 1130-1080 cm⁻¹ regions and the appearance of new lines in the 3403 cm⁻¹ and 1685 cm⁻¹ region, which may be a consequence of chemical transformations in the composite.

An analysis of the composite material using an adhesive liquid was also carried out. After analyzing its structure and porosity, we came to the conclusion that the connection between the VisiJetPXL Core granules is much stronger.

**Conclusion**
After the tests and the microstructure of the product were examined, minerals belonging to the class of sulfates (CaSO$_4 \cdot 2$H$_2$O) and anions of SO$_4$ were found. In addition, polymer chains of the group CH$_2$ and CH$_3$, as well as nitro groups (NH), were found in the composition of the part. It was also found that under the influence of a strengthening liquid, chemical transformations occur in the composite. Due to this, the bonds between the molecules of the composite material become more durable.

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