3D printed glass: surface finish and bulk properties as a function of the printing process

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Abstract

It is impossible to print glass directly from a melt, layer by layer. Glass is not only very sensitive to temperature gradients between different layers but also to the cooling process. To achieve a glass state the melt, has to be cooled rapidly to avoid crystallization of the material and then annealed to remove cooling induced stress. In 3D-printing of glass the objects are shaped at room temperature and then fired. The material properties of the final objects are crucially dependent on the frit size of the glass powder used during shaping, the chemical formula of the binder and the firing procedure. For frit sizes below 250 µm, we seem to find a constant volume of pores of less than 5%. Decreasing frit size leads to an increase in the number of pores which then leads to an increase of opacity. The two different binders, 2-hydroxyethyl cellulose and carboxymethylcellulose sodium salt, generate very different porosities. The porosity of samples with 2-hydroxyethyl cellulose is similar to frit-only samples, whereas carboxymethylcellulose sodium salt creates a glass foam. The surface finish is determined by the material the glass comes into contact with during firing.

1. Introduction

3D-printing, along with other additive manufacturing (AM) and rapid prototyping (RP) techniques, involves building up structures in a layer-by-layer fashion based upon a computer design file. Such techniques are well-suited to the production of one-off, complex structures that would often be difficult to produce using traditional manufacturing methods. There has been rapid growth and interest in this field during recent years, and a range of techniques are now available which make use of many common materials such as plastic, metal, wood and ceramic. However, relatively little has been done to develop AM using glass.

Most commonly today, glass objects are made from a melt. A molten glass blob is taken from the melt and either blown into a mold or free blown. During the blowing process the glass solidifies and, after further cooling, the typical shiny, glassy, surface and an ideally bubble free bulk is achieved. The much older glass-making technique is the so-called kiln glass method, first used by the Egyptians. Glass pieces or frit are filled into a mold and fused in an oven, the so called kiln. In this process, shaping takes place at room temperature and fusing is a second step. The smaller the frit size, the finer the detail on the finished piece but the less transparent it is.

The kiln glass process lends itself to 3D-printing since the printing, i.e. shaping, can be done at room temperature. Direct glass printing methods are powder bed or extrusion methods. The grains of the glass frit are bound together by a binder dissolved in water, for example. The object is then dried. The unfired, but dry, object is called greenware. It is robust enough to be handled but not functional. The greenware undergoes a firing process where the binder is burned off, and the glass grains are melted and fused together. During melting, glass turns into a honey-like liquid. More complex parts need to be supported or even encased to keep their shapes. The support could be understood as a kind of mold which leads us to indirect printing methods.

Indirect methods are methods where the object is not printed directly but a mold or a pattern is made via 3D printing. This approach has been used successfully in jewelry making for at least 20 years and finds more and more acceptance in other applications. The disadvantage of indirect printing is that the complexity of the final object can be restricted by how the mold can be filled. But the advantages are numerous:

1. The material properties of the 3D printed object, either a mold or pattern, are completely separate from and have almost no influence on the final object. A pattern, the object from which a mold is made, can be printed in a variety of materials, for example ABS plastic, wax, silicone or even food stuff. The mold is then made by traditional methods and can be used in traditional ways, either blown glass, kiln methods or casting. The user is

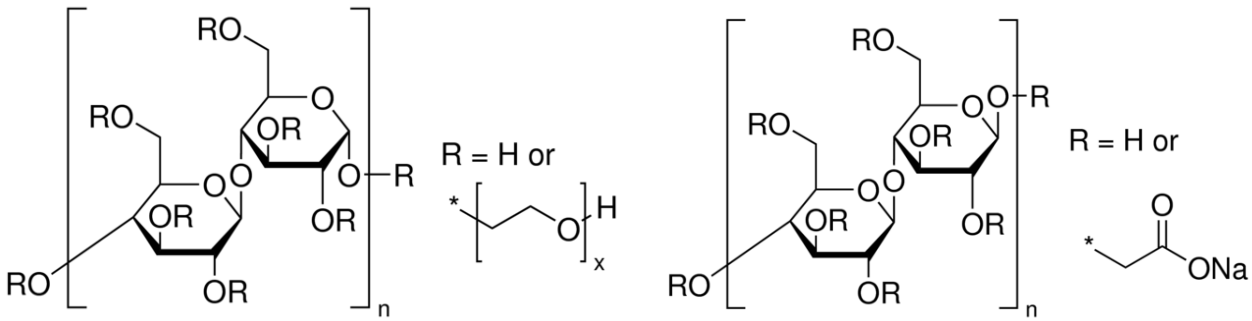
free to use any kind of material for which the mold is suitable. A pattern made out of ABS plastic via a mold made out of plaster can lead, for example, to an object cast in gold.
2. The manufacturing time for multiple objects can be drastically reduced by making multiple molds from one pattern.
3. Direct printing of molds allows new designs which cannot be realized by traditional mold-making methods.
4. Molds and patterns can be post processed; for example, smoothed out. Therefore the amount of post processing of the final objects is reduced.

For glass printing, whether the object is printed directly or indirectly, bulk properties and surface finish depend very much on frit size, binder and firing schedule.

2. Bulk properties

2.1 Bulk properties as a function of binder

The opacity of the final, fired glass object is influenced by both the size of the grains of the glass frit and by the chemical composition of the binder. Here we compare two binders which performed well in pastes used for extrusion printing. The binders are 2-hydroxyethyl cellulose (Sigma Aldrich) and carboxymethylcellulose sodium salt (Sigma Aldrich). Glass frit was supplied by Bullseye and is identified using the product name and code. Figure 1 shows that the chemical structure of the two binders is almost identical.



a) **b)**

Figure1: Structural formula of a) 2-hydroxyethyl cellulose and b) carboxymethylcellulose sodium salt.

After firing samples made with carboxymethylcellulose sodium salt showed much less shrinkage then samples made with 2-hydroxyethyl cellulose and a lighter colour. To explore the difference in appearance we prepared the following samples: 55 wt% of Woodland Brown 0203-08 glass frit /4 wt% of 2-hydroxyethyl cellulose/49wt% of deionized water; 55wt% of Woodland Brown 0203-08 glass frit/4 wt% of carboxymethylcellulose sodium salt/49 wt% deionized water and just Woodland Brown 0203-08 glass frit as a control. Glass, binder and water were mixed until a smooth paste had formed. The paste was rolled out and cut into pieces which were put into a rod pot mold to make rods. The glass powder was simply filled into the mold. All three samples were fired following the firing schedule in Table 1.

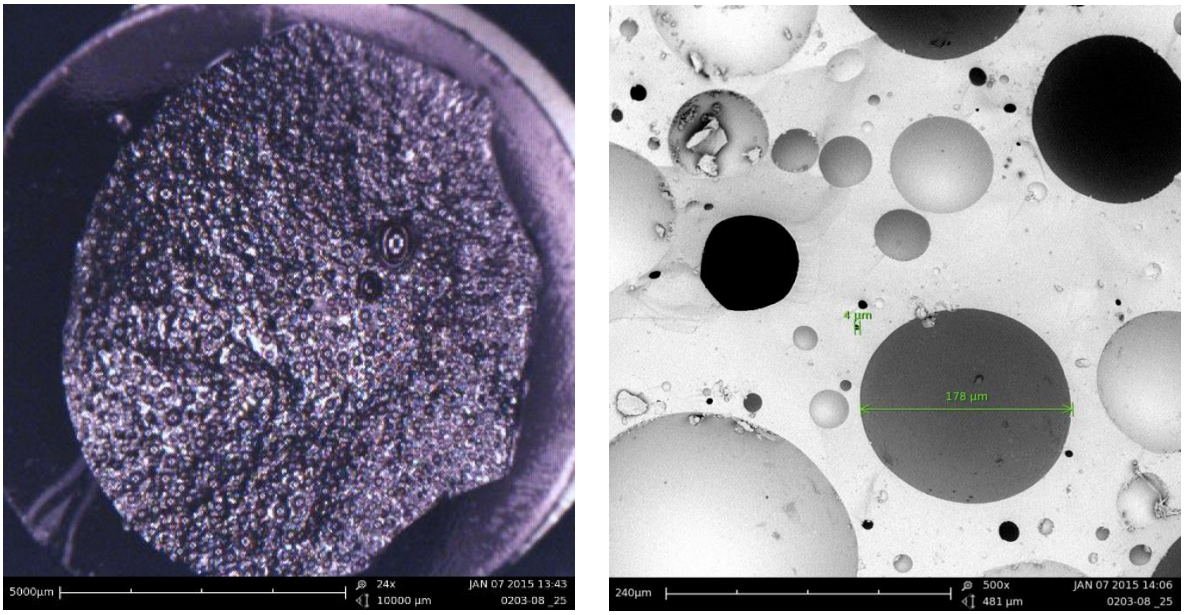
Table 1: Firing schedule

Ramp	100°C/h	to 150°C
Hold at	150°C	for 30 min
Ramp	333°C/h	to 800°C
Hold at	800°C	for 10 min
Ramp	full	to 510°C
Hold at	510°C	for 30 min
Ramp	83°C/h	to 427°C
Hold at	427°C	for 10 min

The first slow ramp and the holding at 150°C for 30 min guarantees that the samples are completely dry.

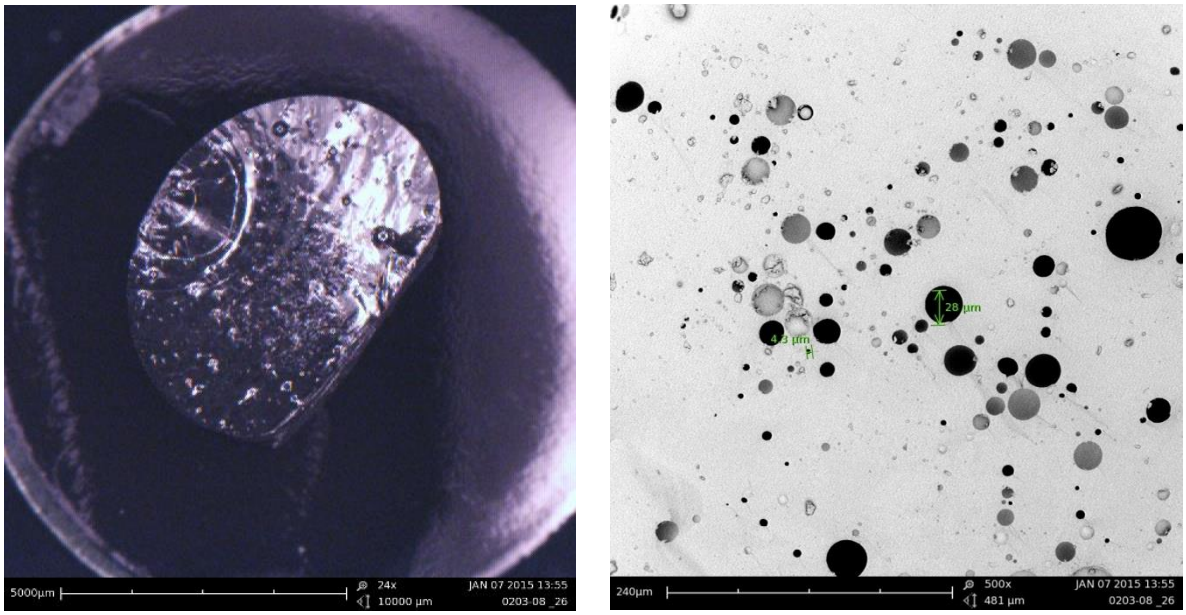
The ramp at maximum cooling rate to 510°C quenches the melt into a glass state. The slow cooling, which follows, anneals the glass samples.

The fired samples were broken into small pieces mounted on studs and sputtered with a 60 nm gold layer to prepare them for scanning electron microscopy (SEM). We used a Phenom desktop SEM to take optical and SEM images.



a) b)

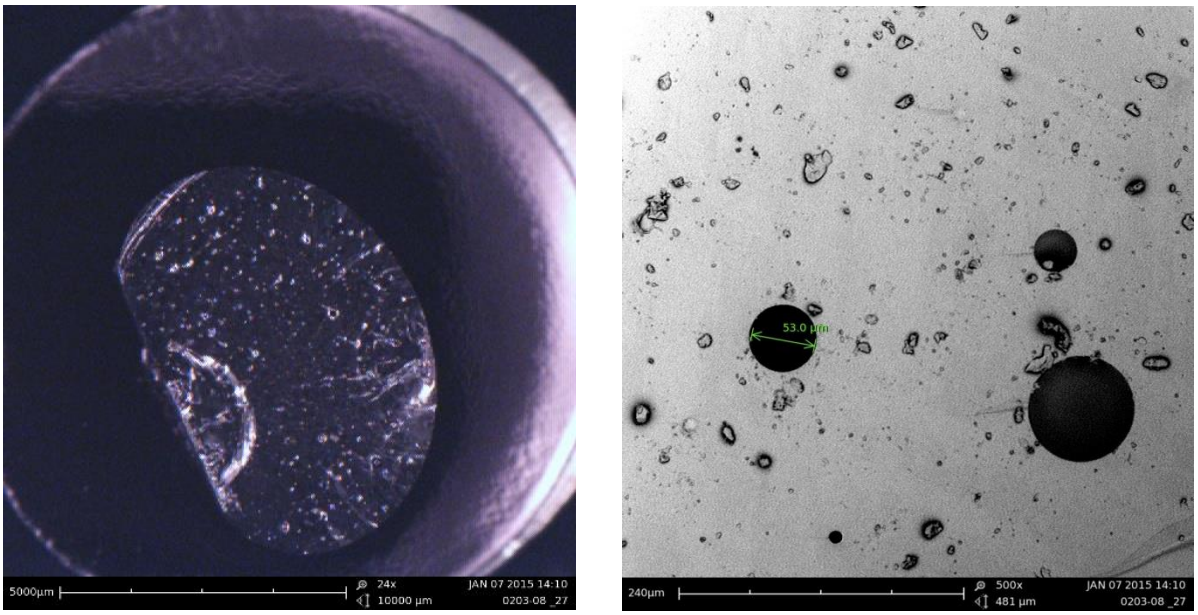
Figure 2: a) optical micrograph of Woodland Brown 2203-08 with carboxymethylcellulose sodium salt as binder after firing following the schedule given in Table 1. b) SEM image at 500x magnification showing bubbles from several hundred microns down to less than 10 microns.



a) b)

Figure 3: a) optical micrograph of Woodland Brown 2203-08 with 2-hydroxyethyl cellulose as binder after firing following the schedule given in Table 1. b) SEM image at 500x magnification showing bubbles in the range of 0.5 to 50 microns.

Samples prepared with carboxymethylcellulose sodium salt form foams with a quite even bubble distribution (see Figure 2). Samples prepared with 2-hydroxyethyl cellulose contain fewer bubbles with a higher bubble concentration in the centre (Figure 3). The lowest bubble concentration is found in the bulk of the powder only sample, but the surface of the sample is covered in huge bubbles with diameters of several centimetres (Figure 4).



a) b)

Figure 4: a) optical micrograph of Woodland Brown 2203-08 only after firing following the schedule given in Table 1. b) SEM at 500x magnification showing only a few bubbles in the size range between 20 to 100 microns.

Carboxymethylcellulose sodium salt clearly increases the number of bubbles in the samples. The huge amount of bubbles leads to less shrinkage, and the lighter colour is the result of scattering at the glass bubble interface. We found the smallest number of bubbles in the frit only sample, but its surface was covered with huge bubbles, i.e. the samples had clearly boiled during the firing process.

2.2 Bulk properties as a function of frit size

As mentioned before, it is well known that the smaller the frit the more opaque the finished glass. The opacity of glass is a function of absorption and scattering. We will concentrate on scattering. It is caused by a refractive index mismatch between the glass and inclusions, most importantly, gas. Figure 5 shows how an increasing frit size leads to less but bigger bubbles until they disappear from the fired pieces. All samples were made from frit only and fired following the schedule in Table 1.

Density measurements of fired glass samples, as a function of frit size and binder, correspond well to the expected value for standard soda-lime glass [1] (2.5 g/cm^3). The majority of samples have densities between 2.3 g/cm^3 and 2.5 g/cm^3. Unfortunately, the error in the measurements is too big to identify a clear trend. Measurement of the Young's modulus for samples with frit size smaller than 250 µm show a decrease as frit size decreases. This is not surprising since the Young's modulus will decreases with increasing porosity [2,3].

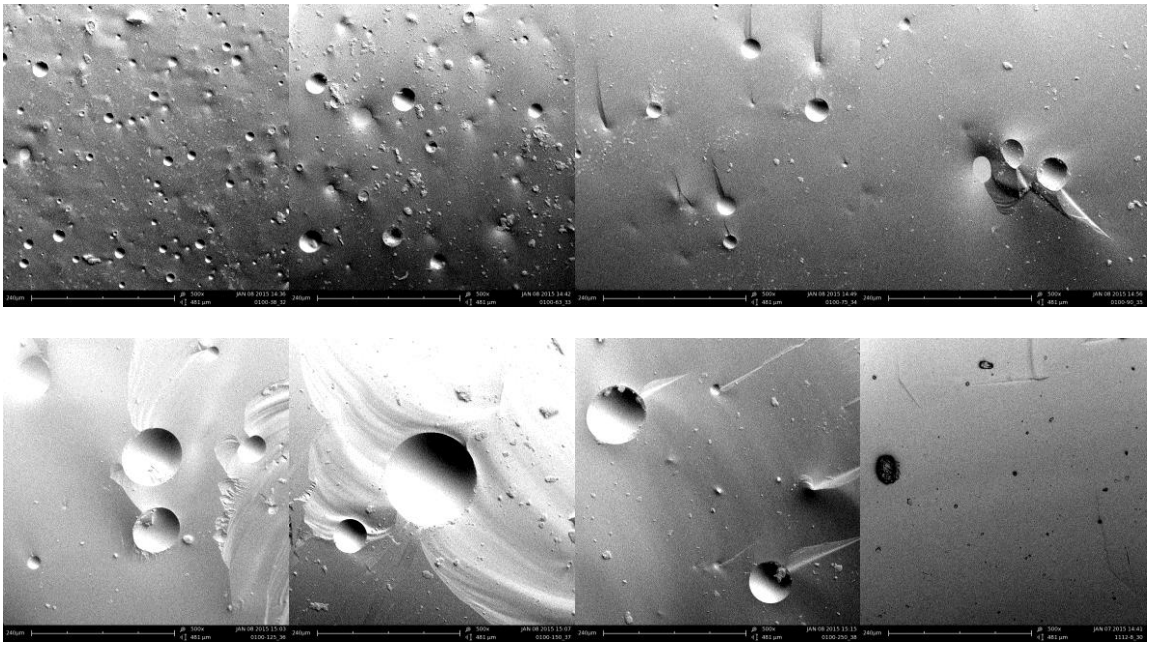


Figure 5: The figure is a collection of SEMs taken at 500x magnification of fired frit samples. All samples were fired following the firing schedule in Table 1. The grain diameters, d, are from left to right, beginning at the top: d < 38 µm, 38 µm <d< 63 µm, 63 µm<d< 75 µm, 75 µm <d< 90 µm, 90 µm <d< 125 µm, 125 µm <d< 150 µm, 150 µm <d< 250 µm, 2000 µm <d< 4000 µm.

Based on [2] we calculated a sample porosity of < 5% of the total volume. This value corresponds well to the SEM appearances of frit-only samples and samples with 2-hydroxyethyl cellulose as a binder. We have not yet done the measurements for samples with carboxymethylcellulose sodium salt as a binder, but expect a much higher value for the porosity. Again, it is difficult to identify a clear trend as a function of particle size. It looks more likely the total volume of all pores stays constant, but the smaller the frit, the higher their number. Figure 6 shows a clear increase of opacity as a function of frit size.

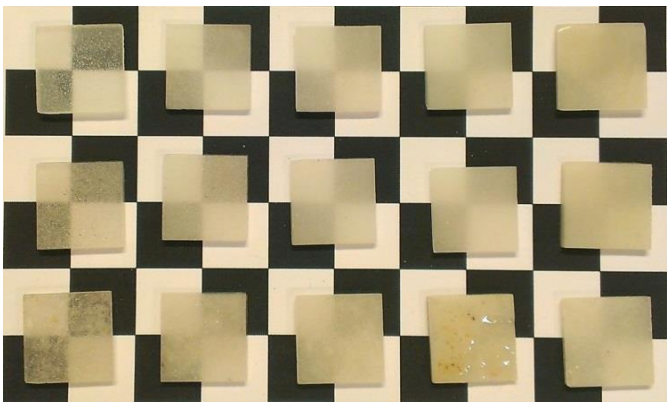


Figure 6: Photograph of uniform glass samples. All samples have a ground finish as a result of cutting. The first row contains samples made out of clear frit only. The samples in the second row were made by mixing glass frit and 2-hydroxyethyl cellulose powder. In the third row the samples were made by mixing glass frit, 2-hydroxyethyl cellulose and water. In all three rows the grain size from left to right is as follows: 150 µm <d< 250 µm, 75 µm <d< 150 µm, 63 µm <d< 75 µm, 38 µm <d< 63 µm, d < 38 µm.

Frit with grain sizes bigger than 250 µm is not suitable for printing. Pastes can be made, but they are too coarse to generate stable greenware. On the other hand, only grain sizes above 250 µm lead to bubble free samples. For transparent glass objects, it is therefore necessary to use indirect printing techniques.

3. Surface properties

Traditionally, glass is associated with a shiny surface which is the result of an air- molten glass interface like in kiln glass production or blown glass production or of a molten metal- molten glass interface like in sheet glass production and of polishing. Contact of the molten glass with rough or structured surfaces will lead to a dull or structured finish. Figure 7 shows a direct print which was supported by two different materials. On the right side, the supporting material was vermiculite, a loose granulate, which allows shrinkage of and airflow around the object. On the left hand side, the support material was plaster. The printed greenware was encased in plaster, by mixing plaster and water and immersing the object into the mixture. After the plaster had hardened, the object was fired in a kiln.

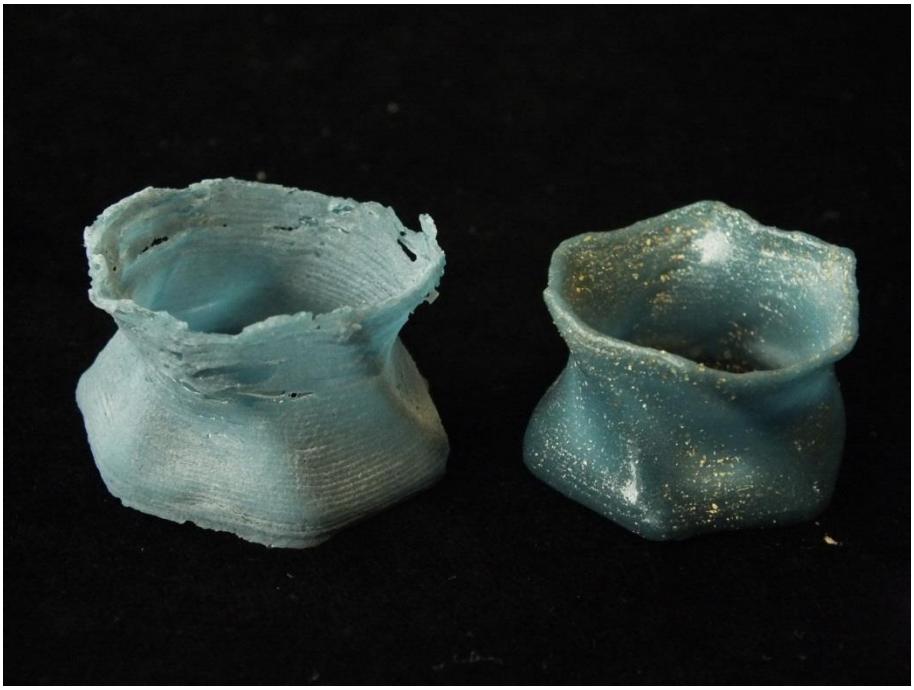


Figure 7: Direct printed objects. The different surface finish is the result of different support materials during firing. On the left side plaster was used. On the right side vermiculite was used.

The plaster encased object shows the printing layers. The sample ripped slightly since the rigid plaster cast did not accommodate for the shrinkage of the sample during firing, causing the thin walls to rip. The surface is dull due to attached plaster.

The objects supported by vermiculite show ‘fire glazing’ since the granulate allowed an air-molten glass interface during firing. The printing layers have smoothed out and the object is smaller in size, since it was free to move in the support material. Some grains have attached to the object.

Figure 8 to 10 show close-ups (optical micrographs and SEM images) of the surfaces resulting from differing support methods, vermiculite, plaster and unsupported. The samples were fired following the schedule given in Table 1, but the maximal temperature was reduced to 730°C since holding at 800°C for 10 min leads to a complete loss of shape when not supported by a plaster cast.

The SEM images were taken using a Phenom charge reducing sample holder. Sputtering with gold was therefore not necessary.
As comparison, we took a SEM image of a piece of glass made by the float glass method (Figure 11). The closest to the surface of the float glass is the sample fired free standing (Figure 8). Under the optical microscope the sample looks smooth and shiny. The SEM revealed that the surface is not really flat, but instead is covered in little pits.

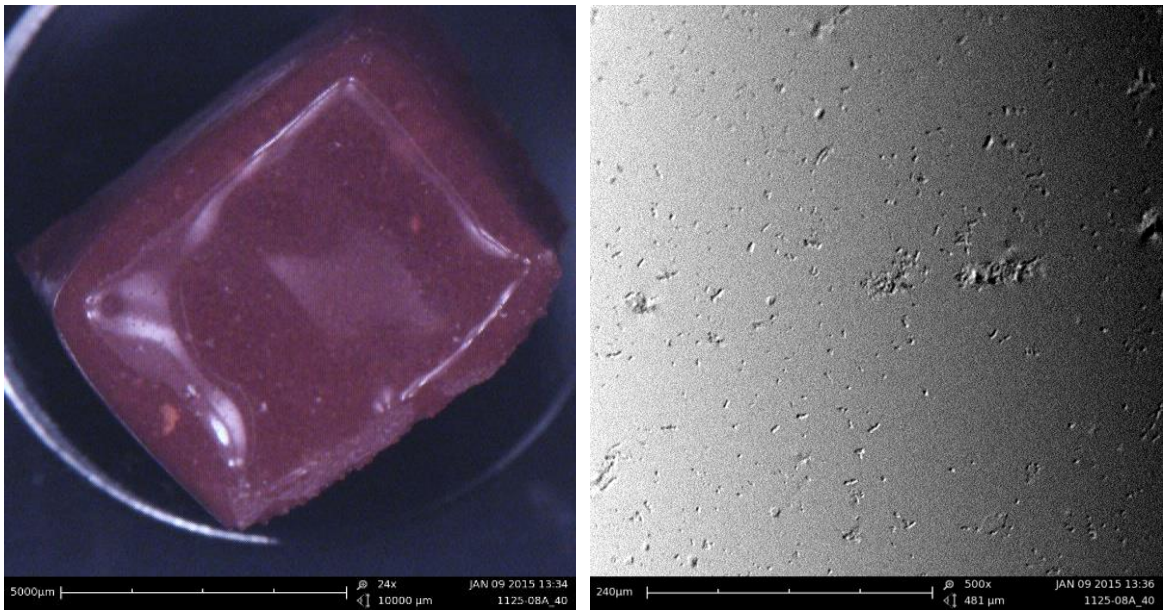


Figure 8: Optical micrograph and SEM image of glass sample, Orange 1125-08, with 2-hydroxyethyl cellulose as binder. Fired free standing,.i.e. without support, at 730°C maximal temperature. The SEM was taken at 500x magnification.

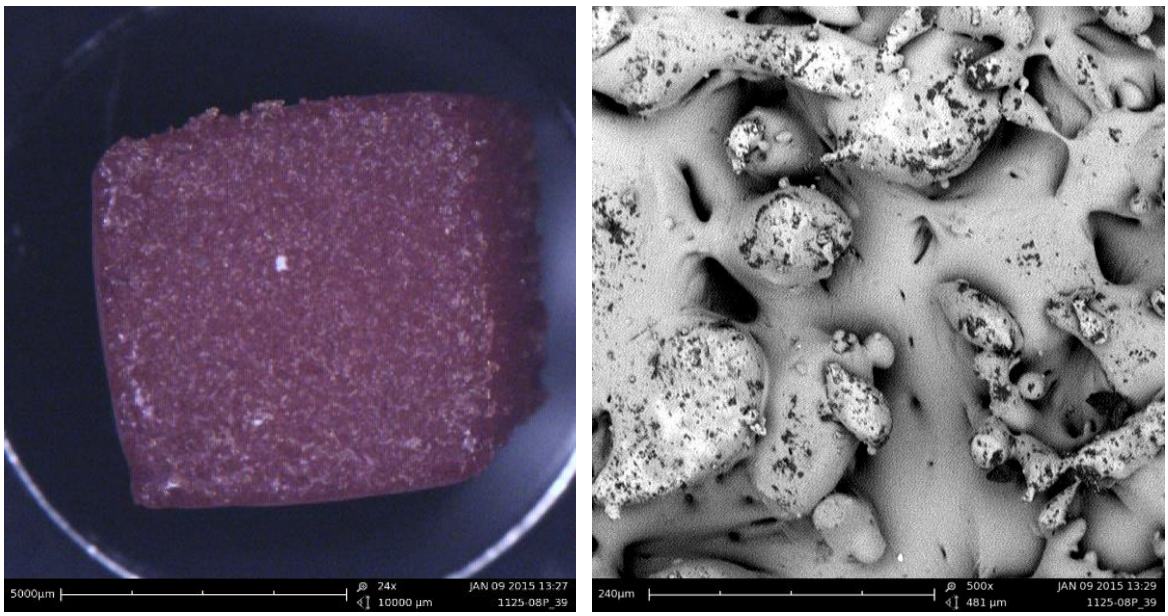


Figure 9: Optical micrograph and SEM image of glass only sample, Orange 1125-08. Fired embedded in a plaster cast at 730°C maximal temperature. The SEM was taken at 500x magnification.

The roughest surface finish occurs when the glass is in contact with plaster (Figure 9). Deep holes and big grains are visible. They could be the result of a temperature reduction by several tens of degrees in the plaster cast. Further investigations are necessary.

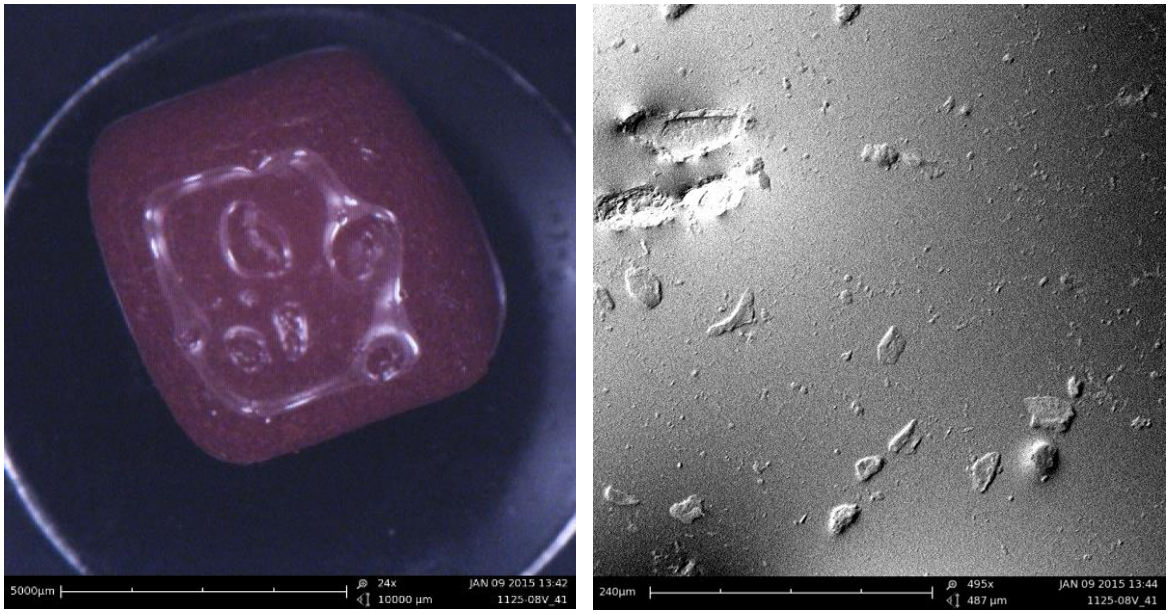


Figure 10: Optical micrograph and SEM image of glass sample, Orange 1125-08, with 2-hydroxyethyl cellulose as a binder. Fired embedded in vermiculite at 730°C maximal temperature. The SEM was taken at 500x magnification.

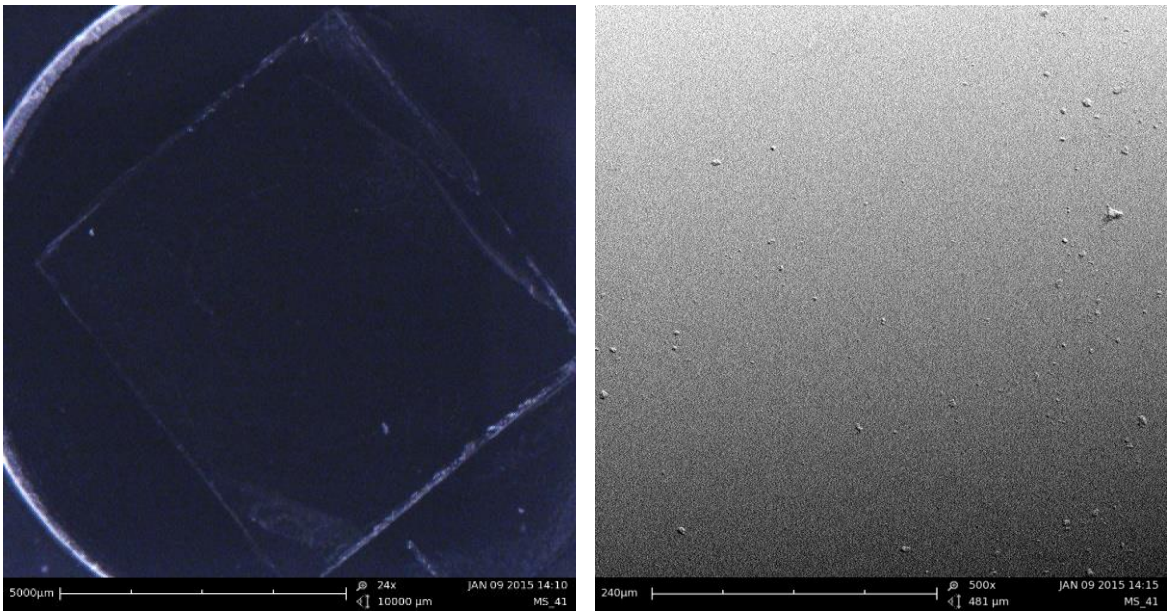


Figure 11: Micrograph and SEM of a piece of soda lime glass made by the float glass method. The SEM was taken at 500x magnification.

The sample embedded in vermiculite shows clear imprints of the granules (Figure 10), even by naked eye evaluation. The surface is smooth but quite contaminated by vermiculite flakes. Even though vermiculite is a material used traditionally in glass bead making as insulating material for annealing, it is not suitable as a support material during firing.

4. Conclusions

When it comes to the optical and mechanical properties of 3D-printed glass the firing step will be as important, if not more important, as the printing step. Frit size and binder define the bulk properties. It remains to explore how a firing schedule with higher maximal temperatures and longer holding times at these temperature influences bubble migration to the surface, and finally degassing of the sample. Whether the object is printed directly or a mold is created, the glass will have an interface with the supporting/ mold material. We will test how the introduction of a releasing agent will influence the surface finish of the fired part.

References

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