3D Printing of Transparent Glass

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Abstract

Traditional assembly line manufacturing is speculative, costly and environmentally unsustainable. It is speculative because it commits substantial resources—energy, materials, shipping, handling, stocking and displaying—without a guaranteed sale. It is costly because each of these resources—material, process, people and place—involves expense not encountered when a product is manufactured at the time of sale. It is environmentally unsustainable because, no matter how much recycling is done, not using the resources unless actually needed is always a better path.

As part of the RAGNAROK (Research on Advancing Glass & Nonorganic Applications to Recreate Objects & Kinetics) project in HP Labs, we identified glass as a promising candidate for additive manufacturing based on 3-D printing methods. Glass is a silica-based material. With 90% of the earth's crust composed of silicate minerals, there will be no shortage of silica resources. Glass is easy to recycle and is environmentally friendly. Glass is inexpensive but looks precious, is pleasant to the touch and is so familiar that customers will not be disappointed by its fragility—under certain conditions.

A major need, and concomitantly a major challenge, for 3D printed glass is transparency. We will discuss several methods how to achieve it.

3D Printing and warm glass

Warm glass or kiln glass is the oldest glass manufacturing method. Glass powder, or frit, is shaped in a mold and fired at moderate temperatures. The powder fuses and a solid glass object is the result. Depending on firing temperature and duration, the glass grains just stick and keep their sandy appearance or melt together and form a smooth body. The major difference between kiln glass and blown glass is that the molten glass mass is not agitated in the kiln glass process. Therefore kiln glass contains many more air bubbles than blown glass. This has consequences for the transparency of the final glass object. The finer the frit, the better the detail but the more prevalently that the air bubbles are trapped. This scatters the transmitted light and turns the object opaque.

3D printing cannot replace the firing process, but does make the mold obsolete. The key to transparency is the 'ink'. We will concentrate on extrusion printing, but the same principals apply to powder bed printing.

There are three ways to suppress scattering and reach transparency: a) index matching between glass grain and solvent, b) big glass grains, and c) small glass grains.

Index match

Glass grains become invisible -- that is, non-scattering – when the solvent they are suspended in has the same refractive index as the glass. Indeed, a suspension of glass in a solution of for example sodium silicate or liquid glass shows reduced scattering. But pastes made like that are not printable. Under pressure, the solution is squeezed out of the paste and jamming occurs. This is a well-known phenomenon easily observed when walking on wet sand on the beach. Firing causes gas formation even with well dried green ware which leads to bubbling of the sample and loss of all detail as shown in figure 1.

Figure1: *Glass sample with sodium silicate solution as the index matching fluid. Firing of the sample leads to bubbling and loss of all detail.*

Big glass grains

Scattering has only little influence on the transmitted light when the diameter of the scatterer is either bigger than ~ 20 µm or smaller than 400 nm, independent of the refractive index difference between scatterer and surrounding medium (see for example [1]). We have found that glass frit with particle sizes between 38 µm and 75 µm results in transparent samples with sufficient detail. In figure 2 air inclusions are clearly visible. Note the choice of binder can have a negative effect on transparency as well. We followed first the recipes published by the University of Washington [2] and added approximately 40wt% of polysaccharides to the glass water mixture. Polysaccharides caramelize at temperatures between 110ºC and 180º. Above 250^{0}C caramel decomposes into carbon mon- and di-oxide, hydrocarbons, alcohols, aldehydes, ketones and several furan derivatives which are volatile [3]. If the caramel is trapped inside the sample, this decomposition is incomplete and leads to a discolouration of the

Figure 2: *Transparent glass sample with air inclusions.*

sample (see figure 3). The polysaccharide content has to be reduced drastically to avoid this effect.

***Figure 3**: For glass sample on the left 40wt% of saccharides were used as binder, for the one on the right only 5wt%. The left on is discoloured, the right one not.*

Small glass grains

As mentioned before scattering should be negligible for particles smaller than 400nm (spherical) diameter. Glass is a brittle material. Milling leads quickly to sub-micron particle sizes. In figure 4 a typical number size distribution is shown. Even though the average particle size is about 700 nm the majority of particles are below 400 nm diameter.

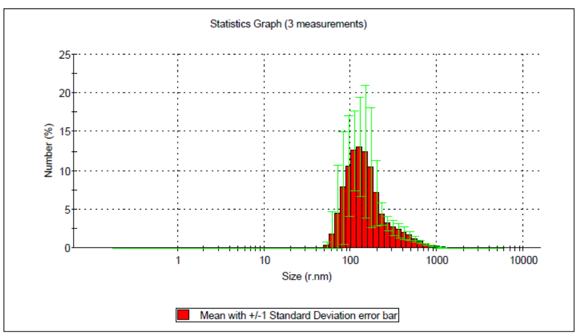

***Figure 4**: Typical number distribution of a milled glass sample. Please note that the x-axis is the radius and not the particle diameter.*

All milled glass samples show excellent detail but are opaque and have an appearance more like ceramic than vitreous appearance. Why?

Density measurements show that sub-micron particles have a random packing after firing, whereas particles with diameters in the micron range have a density so high that the single particles must have melted and flowed together. This result is counterintuitive and demands further investigation. Random packing means that the sample has only ~ 60% of the density of a solid block of glass; the rest is trapped gas. These gas pockets are scatterers in their own right and probably on the order of a micron in size, which leads to the opaque appearance. This assumption will be further investigated.

3D Printing and Cold glass

Cold glass stands for all materials where glass is used in a strengthening component in another cured matrix. The weight percentage of the glass component is only between 5 and 20 wt% and curing does not rely on fusing of the glass particle. First experiments show that the toughness and elasticity of natural polymers change with the amount of added glass frit. A low

***Figure 5**: On the left, the sample is made from particles with an average diameter of 700 nm. On the right, the average particle size was 50 µm. Both samples were fired following the same firing schedule.*

weight percentage of glass reduces shrinkage but the mechanical characteristics of the sample after drying are governed by those of the polymer. The sample becomes tougher but more brittle with increasing glass content. Beyond 50wt% of glass we find a decline in elastic strength. The elasticity of the polymer makes it possible to apply the glass polymer film on elastic substrates. The best results achieved so far are with materials with are index matched to the glass particles. Index matching helps particle dispersion and suppresses scattering independent of particle size.

***Figure 6**: Micrograph of a translucent polymer string with 60wt% glass loading. Glass index and polymer index are matched. The glass particles are not visible but scattering is caused by air inclusions clearly visible as round and elongated bubbles.*

References

[1] H.C. van de Hulst, Light scattering by small particles (Courier Dover publications, 1957)
[2] http://www.washington.edu/news/archive/id/52160
[3] P. Tomasik, “The thermal decomposition of carbohydrates. Part I. The decomposition of mono-, di-, and oligo-saccharides,” Advances in Carbohydrate Chemistry and Biochemistry, 47, 203 (1989).

Author Biography

Susanne Klein holds a Diploma in Physics and a PhD in Medical Physics from the University of Saarland. Since 1995 she has worked and lived in the UK, first as a Royal Society Research Assistant at the University of Bristol and then as a member of HP Labs. Her main research interests lie in new materials for displays and 3D printing.