Thermal and mechanical properties of selected 3D printed thermoplastics in the cryogenic temperature regime

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Abstract. Insulating materials for use in cryogenic boundary conditions are still limited to a proved selection as Polyamid, Glasfiber reinforced resins, PEEK, Vespel etc. These materials are usually formed to parts by mechanical machining or sometimes by cast methods. Shaping complex geometries in one piece is limited. Innovative 3D printing is now an upcoming revolutionary technology to construct functional parts from a couple of thermoplastic materials as ABS, Nylon and others which possess quite good mechanical stability and allow realizing very complex shapes with very subtle details. Even a wide range of material mixtures is an option and thermal treatments can be used to finish the material structure for higher performance. The use of such materials in cryogenic environment is very attractive but so far poor experience exists. In this paper, first investigations of the thermal conductivity, expansion and mechanical strength are presented for a few selected commercial 3D material samples to evaluate their application prospects in the cryogenic temperature regime.

1. Introduction

The application of High Temperature Superconductors is actually expanding to a couple of new fields, in particular space and airborne applications. The design and development of future low or zero emission airplanes is a challenge which requires the integration of the technology of superconductivity, which will be applied in different parts of the vehicle as power generator, electrical combustion drives and transfer lines depending on the philosophy of the approach. The advantage of the high energy density and low losses of superconducting wires and cables allows very compact designs, meets however the disadvantage of a necessary thermal insulation by a containment with vacuum shield, a cryostat, to provide the operation temperature of superconductors and to restrict thermal losses. Such systems are not only expanding the required space but also contribute to the payload of the airplane or space vehicle. Ultra-low weight solutions for superconducting component are not developed so far since they need to use low weight materials, in particular plastics, resins and polymers. Only a limited number of such materials, Polyamides (PA), PEEK, PU etc. are qualified for cryogenic temperatures so far and used. But a large number of other candidates have a good potential and need to be investigated. Plastics, resins and polymers have the disadvantage of a high thermal contraction compared to metals and superconductors, which leads in composites to a thermal mismatch upon cooling to cryogenic temperatures. Dispersion and glass-fiber reinforced are

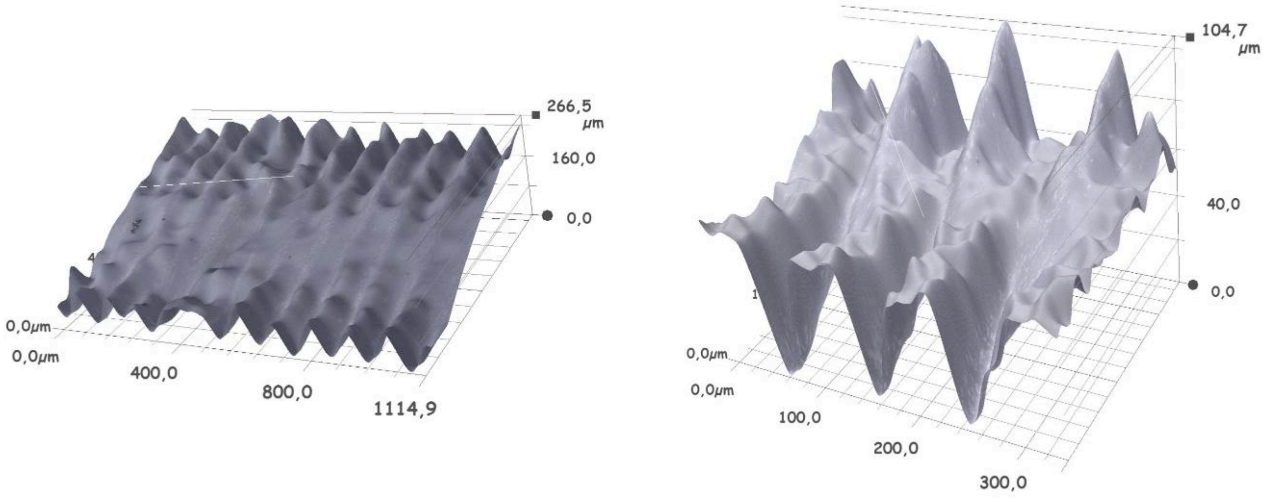

Figure 1. Structure of ABS to investigate the printed layer thickness using the surface profile obtained by optical microscope (left 300x and right 1000x magnification).

materials used to adjust the thermal contraction to those of metals, alloys and composites and to increase the mechanical performance. 3D-printed thermoplastics are so far rarely considered for such cryogenic applications but are promising candidates for complex cryogenic parts and constructions. Rare or no material data on mechanical and thermal properties however are available for this temperature regime. It is the goal of this work to start first investigations of the mechanical properties (tensile stress and compression), the thermal expansion and the thermal conduction on some examples of 3D printed materials to get first data at temperatures in the range of 4-300K.

2. 3D Printing methods of plastics

In this paper the choice of materials was limited to the used printers and therefore to ABS and the photopolymer VeroWhite fullcure 830™, an advanced plastics developed by Stratasys. Two 3D printer with different print technology were used for manufacturing the test specimen. The main difference between the methods is the resolution, layer thickness of the pixels, the densification of the material and the surface and geometry accuracy.

2.1. Fused Deposition Modeling

The first device was a modified Ultimaker-Original for Fused Deposition Modeling, which is an easy

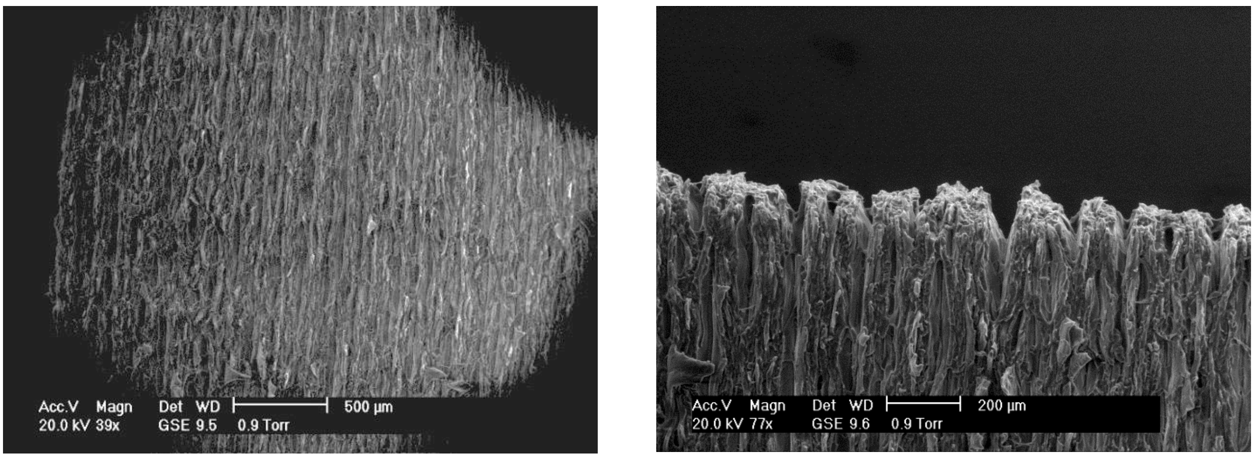

Figure 2. Structure of Polyjet-Modeling material VeroWhite™ to visualize the thickness of the printed layers (pictures by ESEM).

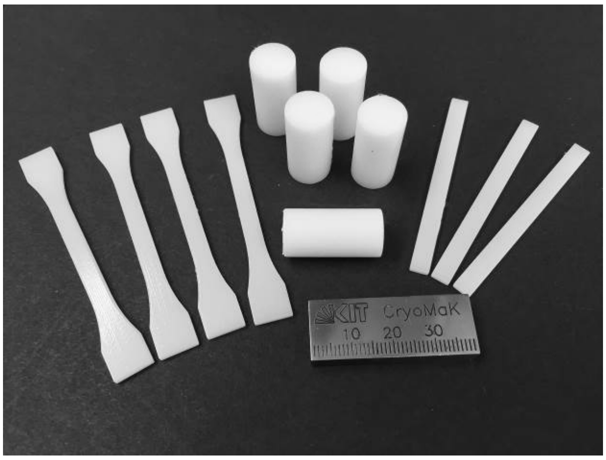

Figure 3. Specimen geometries manufactured by 3D printing method. Shown specimen for tensile (left), compression (middle), and thermal expansion (right) measurement.

and low cost method. The resolution range and sheet thickness is about 100 μm. It allows melting of e.g. ABS (Acrylnitril-Butadien-Styrol) or PLA (Polylactacide) material at ~245°C by depositing on glass plate with a temperature of ~100°C. For this work ABS was chosen. In Fig.1 the layer structure of about 100 μm thickness is visible. The surface has evenly distributed grooves along the deposited sheets with approximately 50 μm depth.

2.2. Polyjet-Modeling
The second approach was Polyjet-Modeling using a Stratasys EDEN 260V device with a resolution in the x,y-plane of ~42 μm with a possible sheet thickness of ~17 μm. The temperature of the system during printing was ~50-60°C. The deposited material is flattened by a roller followed by hardening of the acrylate photopolymer (see datasheet VeroWhite Fullcure830™ [4]) resin performed by UV radiation. This procedure will lead to a more dense body, leak tight regarding liquids [7]. A separate support material can be included into the printed model to create voids. That material can be removed by rinsing with sodium hydroxide solution. Pictures of the surfaces are shown in Fig.2 indicating again the layered structure, indicating a comparable sheet thickness of about 100 μm.

3. Material Properties
To allow an assessment of the cryogenic material properties it was decided to manufacture specimen geometries for thermal expansion, thermal conductivity, as well as mechanical tensile and compressive measurements. In Fig. 4 the shape of the produced specimen by 3D printing method is shown, the dimensions are identical for the ABS and the VeroWhite™ material.

3.1. Thermal expansion
Rectangular beams with a length of about 60 mm and a cross sectional area of about 5 x 2 mm^2 were used to measure the thermal expansion. Details regarding the measurement method can be found in [1, 2]. The contraction behaviour from 290 K down to 4.2 K is depicted in Fig. 5, the typical error is in the range of about 15 μm/m. As expected for such polymers the contraction is in the range of about 12500 μm/m and 15000 μm/m of VeroWhite™ and ABS, respectively. These results in this temperature range are comparable to other plastics like PEI (9100 μm/m), PEEK (10200 μm/m), or PA (13800 μm/m) [2]. On the contrary composite materials like G10 (glass-fibre reinforced epoxy, thermally matched to steel, copper or Nb_3Sn superconductors) exhibit a significant lower thermal expansion due to their glass-fibre addition (normal direction: 6000 μm/m and warp direction: 2400 μm/m) [3]. However, to avoid high mechanical stresses due to a significant mismatch of connected materials, special care needs to be taken.

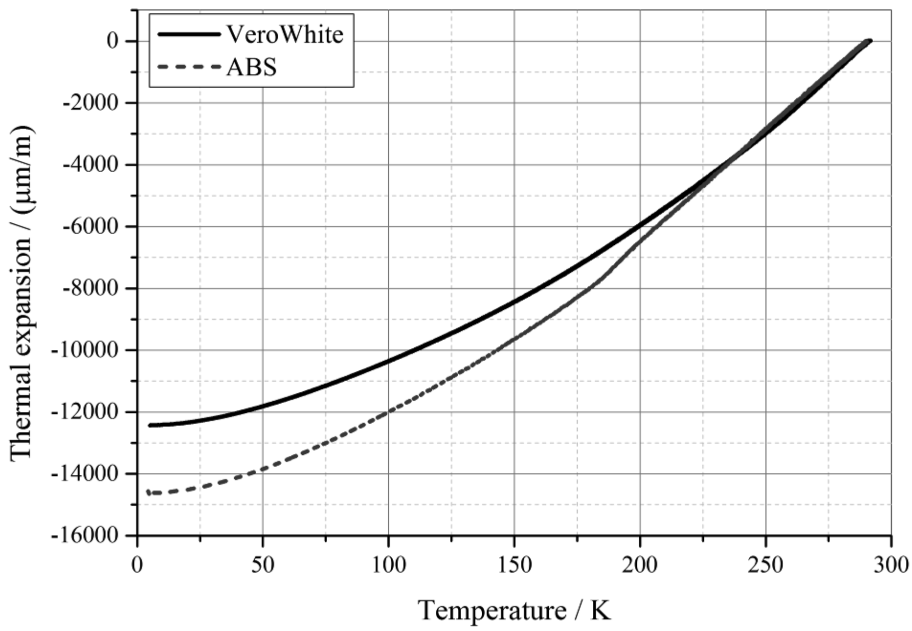

Figure 4. Thermal contraction between 290 K and 4.2 K of ABS and VeroWhite™.

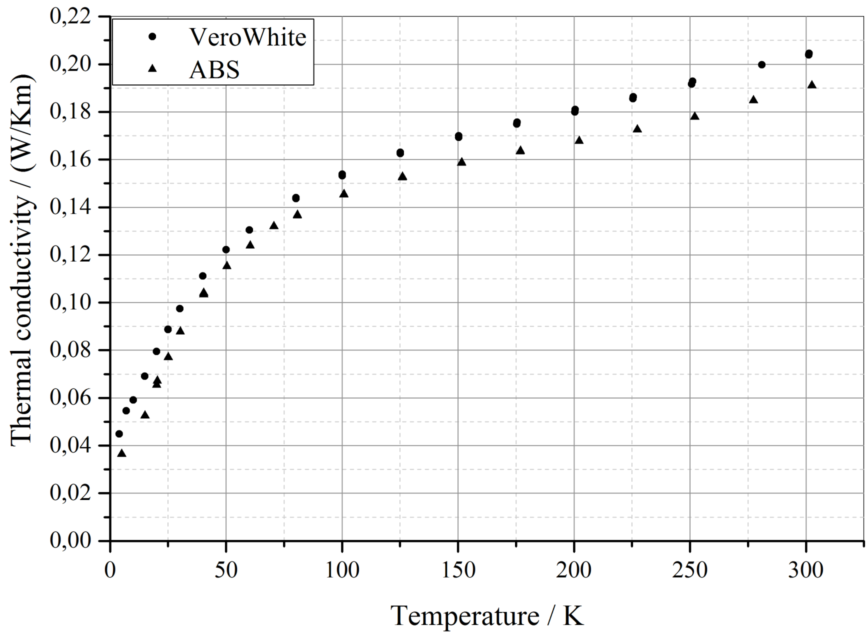

Figure 5. Thermal conductivity between 300K and 4.2 K of ABS and VeroWhite™.

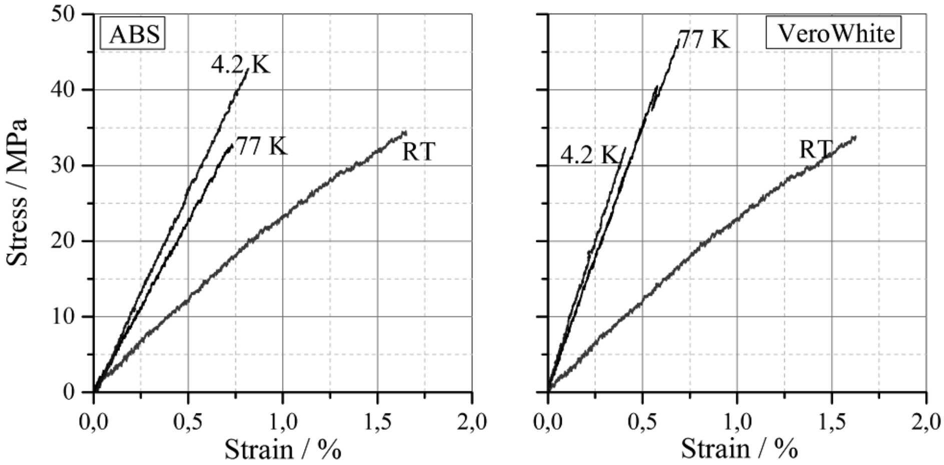

Figure 6. Tensile test results of ABS (left) and VeroWhite™ (right) at RT, 77 K and 4.2 K.

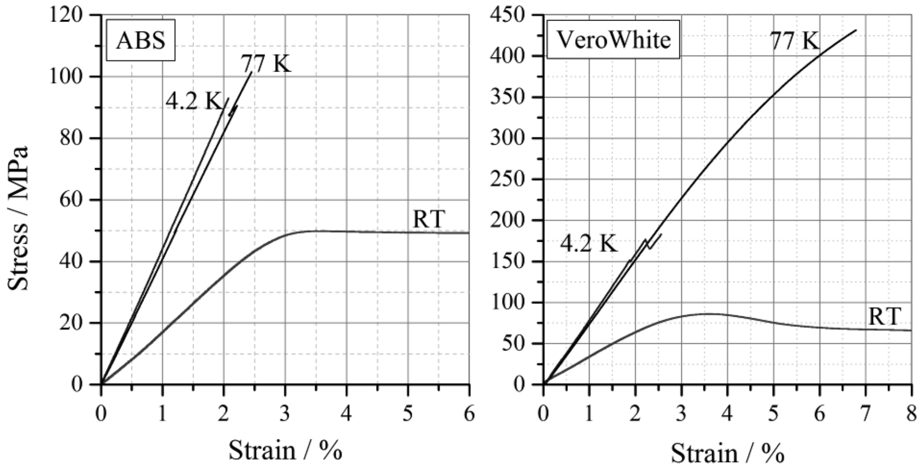

Figure 7. Compressive test results of ABS (left) and VeroWhite™ (right) at RT, 77 K and 4.2 K.

3.2. Thermal conductivity

To investigate the thermal conductivity a *Physical Properties Measurement System PPMS* was utilized [1, 2]. Circular sheets with a diameter of 6 mm and a thickness of up to 2 mm were used to determine the thermal conductivity applying the two-point measurement arrangement. The typical deviation is below 0.01 W/(K m) [2]. In Fig.6 the measurement results are summarized. The thermal conductivity at room temperature is in the range of 0.2 W/(K m) and decreases for both materials to approximately 0.04 W(K m). These low values are expected for such insulating materials. Similar values can be found for pure Araldit or Polyimid (PI, e.g. Kapton) [2]. Compared to G10 composites at 300 K (normal direction: 1 W/(K m) and warp direction: 0.7 W/(K m)) where the glass filler material increases the thermal conductivity slightly [2]. These results encourage the possibility to use such materials as thermal insulators for cryogenic applications.

Table 1. Mechanical material properties tested at RT, 77 K and 4.2 K.

		Tensile			Compressive		
Material	Temp.	Youngs Modulus, GPa	Yield strength, MPa	Ultimate Strength, MPa	Compressive Modulus, GPa	Yield Strength, MPa	Ultimate Strength, MPa
Polyjet-Modeling							
VeroWhite	RT	2.497 (2.5)[a]	32	36 (50)[a]	3.108	81	86
	77K	6.850	-	46	7.813	255	431
	4K	8.876	-	32	7.752	-	183
Fused Deposition Modeling							
ABS	RT	2.583 (2.4)[b]	33	35 (45)[b]	1.591	49	50
	77K	4.476	-	32	4.143	-	101
	4K	5.570	-	43	4.397	-	93

Data at RT from datasheet [a][5], [b][6]

3.3. Mechanical Properties

Beside the thermal properties mechanical characteristics of such materials are of interest. Therefore tensile test specimen were printed and tested according to DIN EN ISO 527-2. Compressive tests were performed on cylindrical 12.7 mm diameter and 25.4 mm high specimen following ASTM D695.

The tests were performed at room temperature of about 293 K (RT), liquid nitrogen temperature (77 K) and immersed in liquid helium (4.2 K). The elastic Young's modulus was determined along with the ultimate strength, and if appropriate the yield strength at 0.2% offset is given. In Table 1 all results are listed. At RT the expected values given by the supplier is added in brackets for information. Taking into account the calculated uncertainty of the obtained values following [8, 9] and a coverage probability 95.45% ($k = 2$) the Young's modulus has $u_E = 1.011$ GPa, the compressive modulus about $u_C = 0.074$ GPa and the yield or ultimate strength $u_{YS/UTS} = 2.120$ MPa. However taking into account the structural integrity, e.g. porosity or interlayer bonding, the estimated uncertainty is significantly higher. Further investigations like reproducibility and micrographs of the cross section area can help to clarify this point. Still, the obtained values are remarkably close to the room temperature values of the supplier.

Looking at the results in Table 1 the typical increase of the Young's Modulus of such materials is found. However, the tensile tests give low strength values around 40 MPa. The largest difference is in the compressive strength, where the VeroWhite™ material is at least double in strength than the ABS for all temperatures measured. This might be attributed to the production route of the Polyjet-Modeling, as each layer of the VeroWhite™ material is slightly deformed by rollers during printing, leading to an increased network structural integrity (see Fig 2).

The same behaviour can be observed in artificially reinforced G10 material [3]. Comparing the obtained values form this work with measurements on G10 material the tensile behaviour normal to the glass-fibres at 4 K is in the same range of about 30 MPa. However due to the reinforcement of the epoxy by glass-fibres the structural integrity is superior in fibre direction (145 MPa). As already stated due to the net structural integrity of the glass fibres, the G10 material exhibits compressive strength values far above 200 MPa allowing the application of such materials for structural reinforcement at cryogenic temperatures.

4. Conclusion and outlook

First investigations on 3D-printed materials for cryogenic temperatures are already promising, although the material choice was limited to the availability of resources for this first step. Two different manufacturing routes (*Fused-Deposition-Modeling and Polyjet-Modeling*) were used to

allow the investigation of the advanced polymer VeroWhite^{TM} with ABS as reference, being aware that ABS is inferior for cryogenic use.
Within this work the samples investigated were printed in the direction of the flat side. An open question is the existence of an anisotropy of properties with respect to the print direction (Fig. 2). Additionally, further tests are necessary to determine the uncertainty of the measured.
The thermal properties obtained show the typical behaviour of such materials leading to very good thermal insulation properties. However, due to the thermal expansion combined with moderate mechanical properties special care has to be taken to avoid failure due to stresses because of temperature gradients during cool down or mismatch of contraction as composite material.
Further investigations regarding the possibility to print composite structures to customize the material properties regarding the needs of specific applications have to be done.
In future the investigations will be extended to a couple of other 3D-printed materials, including investigations on high voltage insulation, thermal cycling, and permeability of gases.

5. References

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