

# 3D Printing Pump Tracks: Improving the Layer to Layer Adhesion through Crystallization Studies.

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**Abstract.** Pump tracks, structures that resemble skate parks, have been 3D printed by ICycle, using rPETG and the Fused Depositing Modeling. They, however, did not present an expected working life, breaking early due to a poor layer to layer adhesion. To improve their performance, the use of glass fiber reinforced PP and SmartAgain® was studied, with two different printing speeds and a previously developed lab scale model, focusing on the crystallization process during printing. The mechanical performance and the glass fiber alignment of the samples were also studied. It was seen that, for both materials, the half-time crystallization curve did not intercept the printing temperature profile, suggesting that crystallization is not completed in the first depositing of material. There is, then, a chance that post-crystallization will occur between the layers. Regarding mechanical properties, SmartAgain® presented a more ductile behaviour, a lower E-modulus and a higher maximum strain, besides deforming more before breaking, making it possibly a suitable material for 3D printing the pump tracks. Polypropylene reinforced with 20% of glass fiber was not recommended for the desired application, since the attempt to print bigger samples with it failed due to warping. Both printing speeds led to similar results, without any significant difference for the tensile and bending tests. The alignment of the fibers could be analysed through SEM, showing that the samples presented isotropy. The mechanical performance for the parallel direction was improved by the fibers, meanwhile for the perpendicular direction they did not show any improvement.

**Keywords.** 3D printing, Additive manufacturing, Fused depositing modelling, Pump tracks, Layer to layer adhesion, Crystallization, Avrami equation, Polypropylene, Polyamide, Glass fibers.

## 1. Introduction

Additive manufacturing processes, or 3D printing, are being increasingly used for different applications and by different sectors. Fused Modeling (FDM) is one of the most common printing techniques, for which layers of material are fused on top of each other, creating an object. When 3D printing, the layer to layer adhesion is one of the factors that must be analyzed and improved since it is directly linked to the quality of the printed object. Certain parameters can influence this adhesion, such as the print speed, the hot end temperature, the feed rate, the cooling and the layer height. Considering only the printer settings, without changing the material used, two major factors can be pointed out: the flow efficiency ( $F_E$ ), which is the ratio of the amount of plastic that was actually extruded and the calculated amount, and the sublayer temperature, which can be changed by variations in the extrusion temperature, the feed

rate, the cooling and the layer printing time<sup>[1]</sup>.

Another process that has to be considered, when 3D printing semicrystalline polymers, is the crystallization during the cooling of the printed object. Crystallization, depending on when and how it occurs, can either improve or weaken the layer-to-layer adhesion. If each layer crystallizes separately, the final product will not have a great bond between its layers. In contrast, if the crystallization happens in a way that links the layers together, i.e. the crystalline region goes beyond the boundary of a single layer to the next layer, the adhesion between layers will be enhanced and the printed object will have improved mechanical properties<sup>[2]</sup>.

During printing, the polymer leaves the extruder with a temperature higher than its melting temperature and lays down on the print bed, which has a much lower temperature. Besides this, the elongational flow present during the deposition

process causes the chain to experience a molecular orientation that can favour the crystallization of the material [3]. Also, as the printing proceeds by adding new filaments from the melt in successive layers, the layer that has already been deposited is reheated, possibly inducing cold crystallization[2]. To analyze the crystallization during printing, the temperature profile can be overlaid by the polymer's isothermal crystallization curve, making it possible to predict if there will be enough time, at a suitable temperature, for the material to crystallize[2].

To analyze polymer crystallization, the Avrami equation, which describes how a material transform from one phase to another at constant temperatures, is often used. Its simple form, considering a constant nucleation rate and constant linear growth, can be expressed as equation (1), where  $V_c$  is the relative volumetric transformed fraction,  $n$  is the Avrami index and  $k$  is the overall crystallization rate constant. The Avrami index is composed of two terms:  $n_d$  (dimensionality of the growing crystals) and  $n_n$  (time dependence of the nucleation). The term  $n_d$  can only have as values the integer numbers 1, 2 or 3, leading to one-, two- or three-dimensional entities that are formed [4].

$$1 - V_c(t) = \exp(-ktn) \quad (1)$$

The crystallinity,  $X_c$ , can be calculated by equation (2).  $\Delta H_m$  is the melting enthalpy and  $\Delta H_{cc}$  is the cold crystallization enthalpy, relative to the enthalpy of a theoretically 100% crystalline polymer. The heat of formation,  $\Delta H^0_f$ , is given for each material[2].

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^0_f} * 100 \quad (2)$$

For this project, a partnership between Zuyd Hogeschool, Chemelot Innovation and Learning Labs and Icycle, the OpZuyd Circular Polymer Project, was set, so 3D-printed pump tracks could be studied. A pump track resembles a skate park and, without pushing off or pedalling, it is possible for the pump track's user to drive "pumping" through the track. They are usually built with a lot of materials, like concrete, asphalt and wood. Trying to innovate in this area, through sustainability, Icycle, also named Velosolutions Benelux, has decided to build them with recycled materials, using 3D printers. Some pump tracks have already been printed with recycled polyethylene terephthalate glycol (rPETG), but they do not have the expected working life. It is often noticed that its structure breaks in between the printing layers, leading to the conclusion that the layer to layer adhesion is not strong enough.

To easier analyze if it is possible to improve these pump tracks, Vranken, 2021 [5], settled a guideline for lab-scale printing with rPETG through analyses of temperature and mechanical properties of production-scale samples. At the production scale, equilateral triangles were printed (40 cm length per side and 60 print layers) with different cycle times and temperature measurements were taken. It was seen that faster printing led to a higher temperature profile so that the temperature of the material

remained higher (above Tg) for a longer time. When testing on a lab scale, it was not possible to print smaller triangles, so a rectangular structure (40mm length) was printed at two different speeds. Temperature measurements were also taken and the results were similar to the previous ones: higher print speeds led to a higher temperature profile For testing the mechanical properties 1BB bars were cut from the rectangle structure (lab scale) in two different directions: parallel and perpendicular. It was concluded that the translation from the lab scale to the production scale was quite successful. The highest achieved values for E-modulus, maximum stress and maximum strain for both the lab scale and the production scale were similar, mainly for the perpendicular direction.

Seeking to compare the 3D printing of rPETG with other polymers and to further improve the pump tracks, this study was developed, utilizing different recycled materials: fiber glass-reinforced polypropylene (PP) and SmartAgain®, made with polypropylene and polyamide (PA6). The main goal is to discover how to make better 3D printed pump tracks, in terms of their mechanical properties, by changing the printing settings and the polymer used. Since it is already possible to get the same mechanical values at the lab scale as at the production scale [5], lab scale experiments, printing with fiberglass-reinforced PP (20% and 30% of fibers) and SmartAgain®, have been performed.

## 2. Methodology

### 2.1 Sample Preparation

For this study, rectangles with a length and a high of 40 mm were printed at two speeds (40 mm/s and 70 mm/s), using an Ultimaker S5 FDM 3D printer with a nozzle diameter of 0.8mm and no bed heating. To perform bending tests, bigger samples, with dimensions according to the middle part of 1A bars, were printed at 40 mm/s and at 70 mm/s. An attempt was made to print these bigger samples using all three materials, but PP 20% GF presented a lot of warping, causing the attempts to fail.

Polypropylene samples were injection molded in 5A bar shape so they could be subjected to tensile test and the influence of the glass fiber on the mechanical properties could be better understood. A Boy injection molding machine was used, with a temperature close to 225 °C and a mold temperature equal to 30 °C.

### 2.2 Thermal Measurements

To obtain the temperature profile, temperature during printing was measured, with a thin K thermocouple registering the temperature every 100 milliseconds. The thermocouple was attached to the printing bed and the two printing settings were measured (40 mm/s and 70 mm/s). Every time the nozzle ran over the thermocouple the heat transfer was recorded as it migrated through the layers.

Differential Scanning Calorimetry (DSC) was used to study isothermal crystallization. Samples of each polymer were heated to a temperature above its melting temperature (220 °C for PP and 250 °C for SmartAgain®) and held so for 5 minutes. Afterwards, they were quickly cooled down, at 50 °C per minute, to 145 °C and held isothermal for 60 minutes. Then, they were cooled to room temperature and heated again to 220 °C or 250 °C (depending on the polymer) so the process could be repeated. This time, though, keeping the sample, after quickly cooling, at 140 °C instead of 145 °C. The same was done a few times, cooling the sample to temperatures of 5 °C apart until they were cooled to 110 °C. The data obtained were plotted on a graphic of heat flow vs time and the interesting region (where the crystallization peaks can be properly seen) was defined, so the same process could be done again. For PP, the DSC was done for the second time with isothermal temperatures between 147.5 °C and 125 °C and steps of 2.5 °C and for SmartAgain® between 132 °C and 118 °C with temperatures 2 °C apart. It was then possible to determine the half-time of crystallization and analyze it with the temperature profile.

When the samples were already printed, they were also analyzed by DSC, so their crystallinity could be better known and compared. A heating program was used, heating the PP samples to 220 °C and the SmartAgain® samples to 250 °C, both at 10 °C per minute.

### 2.3 Tensile and Bending Test

For the mechanical tests, a Zwick/Roell machine was used. To perform the tensile tests, 1BB bars, according to ISO 527-2, were cut in two different directions from the wall-printed samples. The pre-load was equal to 0.1 N, and the speed for the tensile modulus was 0.125 mm/min and thereafter 5 mm/min. Also, injection-molded 5A bars were tested, with a 0.25 N pre-load, a tensile modulus speed of 0.3125 mm/min and a further speed of 12.5 mm/min.

For the bending test, 1A bars were used, with a pre-load of 0.2 N, a speed for the tensile modulus equal to 2 mm/min and after that to 10 mm/min. For both tests (bending and tensile) at least 5 specimens were tested.

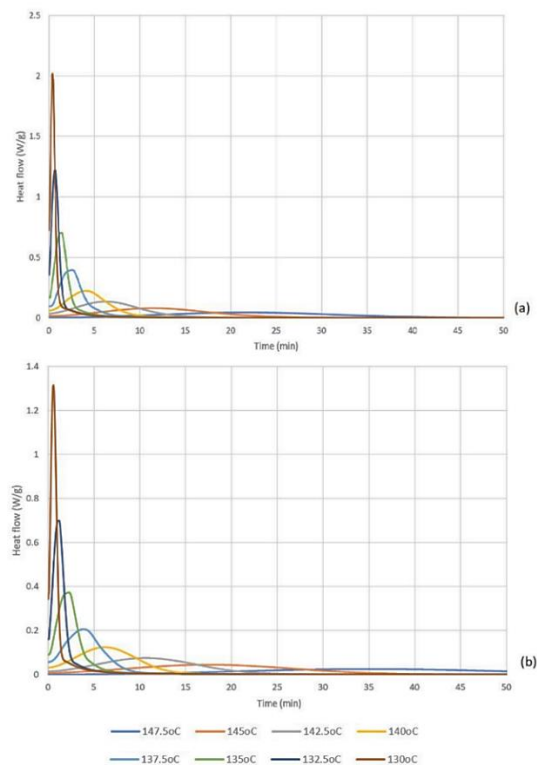
### 2.4 SEM Analysis

Scanning Electron Microscopic (SEM) was used to optically evaluate the samples. For this, they were cooled with liquid nitrogen, so polypropylene could be in a glassy state, and then broken. The fractured parts were taped to a stage using carbon tape and images were taken. Only PP 30% GF samples were assessed through this method, since the main goal was to look at the glass fibers (which are not present in SmartAgain®). PP 20% GF was not analyzed because the fibers should have the same alignment as PP 30% GF.

## 3. Results and Discussions

### 3.1 Polypropylene

Crystallization dynamics were studied through DSC. For this, the heat flow vs time graph was plotted, as can be seen in **Figure 1**.



**Figure 1** - Heat flow vs time graph for PP20% GF (a) and PP 30% GF (b)

Since crystallization started before the isothermal temperature was reached, the heat flow vs time curves are incomplete, making it impossible to determine the crystallisation half-time via the standard route. Therefore, the half-time of crystallization was determined in two alternative ways. One way is applying the Avrami equation, for which the  $n$  and  $k$  index must be determined and the area under the curve that represents 50% of the total can be calculated using equation 1. The other one is looking to the maximum point of the peak, which should give the half-time of a symmetrical peak.

Both methods gave comparable results for the half-time, which decreased when the isothermal temperature decreased as well. The rate of crystallization was higher for lower temperatures and PP 20% GF presented faster crystallization. Polypropylene with 20% glass fiber also presented a higher value when looking at crystallinity. For this, DSC with printed samples was done, with just a first heat curve. The crystallinity was calculated using equation 2 ( $\Delta H^0_f$  equal to 207.1 J/g for PP) in two ways: considering the material in general, with glass fiber, or considering just the polymer. For the first one, the  $\Delta H^0_f$  is 207.1 (100% PP), but the maximum  $X_c$  that can be achieved is 80% for PP 20% GF and 70% for PP 30% GF. The second one can lead to

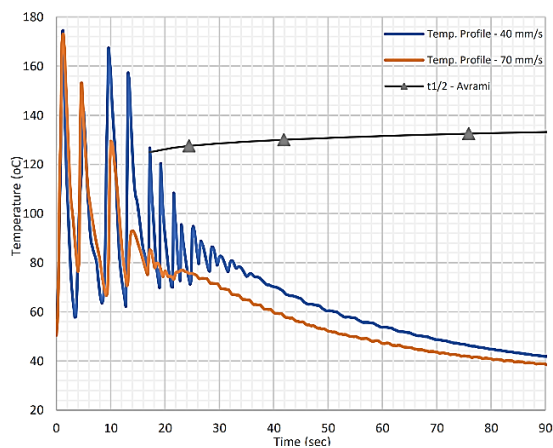
values of  $X_c$  equal to 100%, but the  $\Delta H_f^0$  has to be corrected (80% of the mentioned value for PP 20% GF and 70% for PP 30% GF). **Table 1** summarizes these values.

**Table 1** - Crystallinity values for polypropylene printed samples.

	Material	Enthalpy (J/g)	Crystallinity (with GF)	Crystallinity (without GF)
PP 20% GF	40 mm/s	65.3	31.53%	39.41%
	70 mm/s	62.9	30.37%	37.96%
PP 30% GF	40 mm/s	50.6	24.42%	34.88%
	70 mm/s	52.1	25.15%	35.93%

The slight difference between PP 20% GF and PP 30% GF crystallization could be explained by the effect of the glass fibers or by differences in the polymer matrix. Tarani et. al, 2019<sup>[6]</sup> saw that GF retarded the crystallization by the formation of a rigid amorphous phase in the material that restricted chain mobility and did not enhance the crystallization rates. Assuming that the matrix was the same for the two batches of PP, this could be a reason for the lower crystallinity of PP 30% GF.

To better understand how crystallization occurs, the temperature profile, obtained after temperature measurements, was plotted together with the half-time of crystallization for polypropylene 30% GF. This graph is shown in **Figure 2**, with the half-time obtained with the Avrami equation plotted.



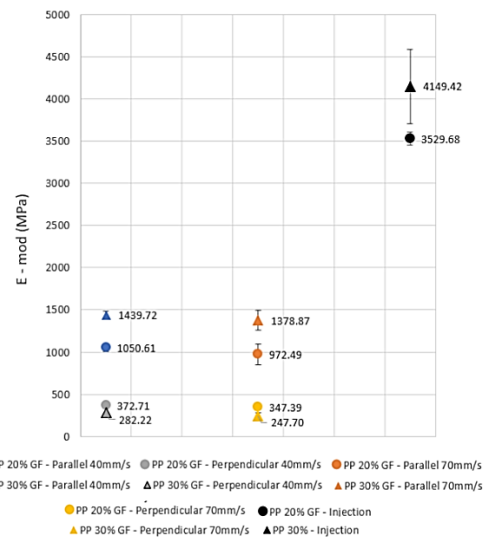
**Figure 2** - Temperature profile and crystallization curve for PP 30% GF.

As can be seen, the measured temperatures were lower than the ones set on Cura, since the material cooled really fast after leaving the nozzle and there was some delay in the heat transfer between the material and the thermocouple. After a few layers, the temperature dropped to a value lower than 50 °C and the deposition of a new layer could not interfere much anymore with the temperature measured, so the measurement was stopped. It can also be noticed that, for the first two layers, both speeds resulted in similar profiles, but when more layers were being deposited, slower printing resulted in higher temperature peaks. When slower printing, the nozzle

takes more time to move away from the thermocouple, improving heat transfer. On the other hand, faster printing make it harder for the heat to transfer between the layers, since the nozzle moves faster from the point where the thermocouple is attached.

Regarding the crystallization dynamics, it can be seen that the half-time crystallization curve did not intersect the temperature profile for the first peaks, suggesting that the initial crystallinity after deposition is likely to be low. Since there is no time for the material to completely crystallize in the first deposition, the chains could move in between the layers and, when the next layer is deposited, post-crystallization can be induced, leading to a stronger bond among the layers<sup>[2]</sup>. However, since crystallization started too fast, it was not possible to measure the half-time for lower temperatures through DSC. If the entire curve had been obtained, it is possible that it would intersect the temperature profile for the first peaks, leading to a different conclusion.

Mechanical properties of the samples were tested through the tensile test. 1BB bars were cut from the wall samples in two directions and 5A bars were injection molded. The results, presented in **Figure 3**, show that perpendicular specimens result in lower values, which could be explained by the layer-to-layer adhesion, considering the direction of the force applied during testing. The chosen printing speeds resulted in similar values, probably because the layer time was short for both speeds, leading to similar printed structures, which can also be seen through the similar  $X_c$  values shown in **Table 1**. Student t-test was performed and, indeed, there was no significant difference for all three parameters when changing the speed.

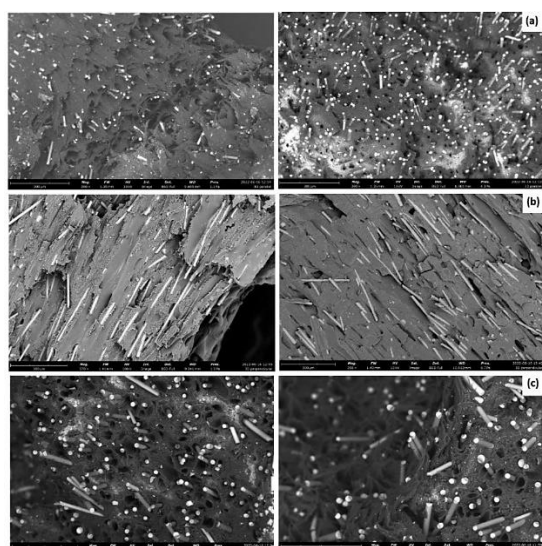


**Figure 3** - E-modulus results for polypropylene.

Regarding the injection molded 5A bars, a considerably higher E-modulus was found. This difference was expected, since injection molded products are usually stronger than 3D printed ones, as they are made from a single poured layer of

plastic, instead of a lot of thin slices placed on top of each other. From SEM, as shown below, it was possible to see that the fibers were mostly orientated in the direction that would increase the modulus, explaining why PP 30% GF presented the higher value.

It can also be seen that the E-modulus was higher for PP 20% GF for the perpendicular samples compared to the 30% GF samples, but the opposite is found for the parallel samples. Two factors influence the E-modulus: the amount of glass fiber and the crystallinity. Fiberglass reinforced polymers exhibit isotropy, making the tensile behavior dependent on the direction of applied stress. If the fibers are tested in a way that the stress is parallel to them, the maximum tensile strength is achieved. If the stress is applied perpendicular to them, there is no enhancement and the tensile strength of the matrix may be reduced<sup>[7]</sup>. Crystallinity also influences E-modulus, since a semi-crystalline polymer is a two-phase material and the presence of crystals leads to an increase in modulus (the crystals in the amorphous phase behaves like crosslinks and produce stiffening). Also, a semi-crystalline polymer behaves as a composite, so the modulus observed is a result of the combined modulus of the amorphous and crystalline regions<sup>[8]</sup>. To better understand the results, SEM pictures were taken, as presented in **Figure 4**, and the orientation of the fibers could be seen. The glass fibers lie in the parallel direction, explaining the higher E-modulus for the polypropylene with more fibers (30%) when testing the parallel specimens. The fibers could not improve the mechanical performance for the perpendicular samples, so the material with more crystals, PP 20% GF, presented a higher E-modulus.



**Figure 4** - SEM pictures for polypropylene samples (a) 3D printed parallel direction, (b) 3D printed perpendicular direction and (c) injection molded.

Bending test was also performed, since the pump track is often bent, instead of pulled. It is not possible to perform bending test using 1BB bars, thus the middle part of 1A bars was 3D printed. As mentioned,

the attempt to print these new samples with PP 20% GF failed due to warping, which points out the difficulty of using it to print large objects, such as the pump tracks. **Table 2** shows the average of the found results. A student t-test was also done and no significant difference when changing the speed was found. Bending results also show that glass fiber reinforced polypropylene behaved as a brittle material, since it could not be significantly deformed either elastically or before fracturing.

**Table 2** - Bending test results for polypropylene 30% GF- E-modulus, maximum stress, maximum strain and strain at break.

Speed	E-mod (MPa)	$\sigma_{fM}$ (MPa)	$\epsilon_{fM}$ (MPa)	$\epsilon_{fB}$ (MPa)
40 mm/s	1653.80	38.06	2.91	4.86
70 mm/s	1710.22	36.68	3.07	4.41

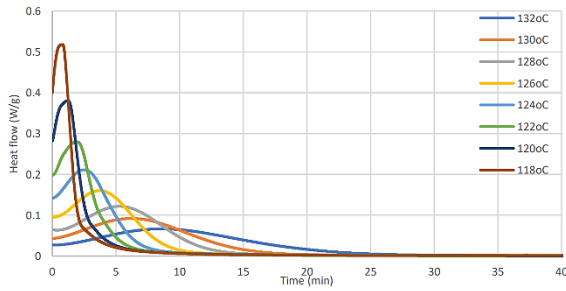
The found bending E-modulus is comparable to the one from the 1BB parallel bars tested through tensile, being slightly higher. The way the fibers are oriented during printing also suggests that, as for the parallel bars, the fibers will not improve the modulus for the bending test and the way the parallel bar was cut from the wall resembles the way the 1A bar was printed, flat on the build plate. It is important to point out that the temperature profile shown for the wall samples should not be the same for the 1A bars and this difference could also mean that each sample will crystallize differently, making it hard to compare their properties.

Considering all results found for the glass fiber filled samples, it was concluded that polypropylene 20% glass is not recommended for printing pump tracks, since warping has made it unfeasible for bigger samples to be printed. PP 30% GF did not show the same problem, but it behaved in a brittle way, which could be a problem for the studied application. The glass fibers were seen to influence the mechanical properties and, if they were aligned in a parallel way to the applied stress, the E-modulus was increased. Regarding crystallization, it was seen, with the data obtained until now, that polypropylene did not completely crystallize with the first deposition of material, making it possible for the crystals to form in the inter-layer region.

### 3.2 SmartAgain®

SmartAgain® crystallization dynamics were also studied through isothermal DSC. The heat flow vs time graph is presented in **Figure 5**. The same trend observed for polypropylene, regarding the behavior of the half time with the temperature, was found for SmartAgain®: lower temperatures presented shorter half times. However, it can also be noticed that SmartAgain® crystallized slower, when compared to PP. For the same temperature (130 °C), PP had less than one minute as half time, but for SmartAgain® this took considerably more time.





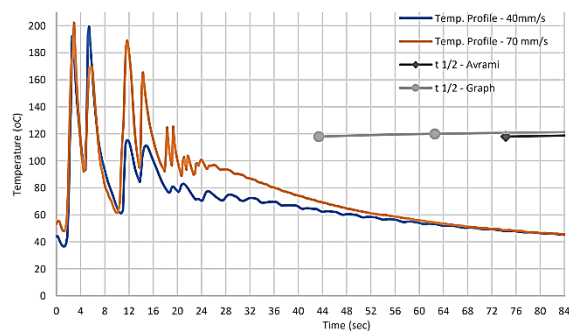
**Figure 5** - Heat flow vs time graph for SmartAgain®.

The crystallinity was, again, studied through DSC, heating the printed samples.  $X_c$  was calculated by equation 2, where  $\Delta H^0_f$  is equal to 207.1 J/g for PP and to 230.1 J/g for PA6. SmartAgain® has 60% of PP and 40% of PA6, so the heat of formation should be corrected. **Table 3** summarizes these values.

**Table 3** - Crystallinity values for SmartAgain® printed samples.

Printing speed		Enthalpy (J/g)	Crystallinity
40 mm/s	PP	32.279	25.98%
	PA6	21.369	32.22%
70 mm/s	PP	32.402	26.08%
	PA6	21.652	23.52%

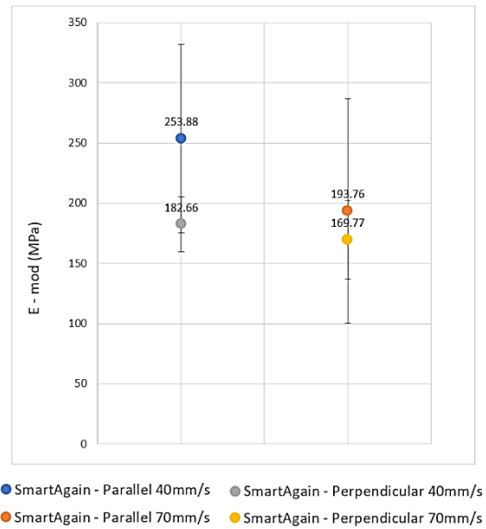
SmartAgain® crystallization during printing was studied through temperature measurements. **Figure 6** shows the temperature profile plotted together with the half-time obtained with isothermal studies. It can be noticed that the crystallization curve did not intersect the temperature profile, as for polypropylene, suggesting that the crystallization was not complete in the first deposition and there was time for the chains to move in between layers. When the second layer was deposited, it was still possible for SmartAgain® to crystallize and, if this post-crystallization occurs in an inter-layer way, the bond would be improved. Other than what was observed for PP, faster printing resulted in higher peaks after a few layers. When the measurements were taken, warping was noticed, which may affect heat transfer, explaining this trend.



**Figure 6** - Temperature profile and crystallization curve for SmartAgain®.

The mechanical properties of SmartAgain® were also studied through tensile test. Results, which can be seen in **Figure 7**, show that the printing speed did not present a considerable influence on the printed

samples. After a Student t-test, it could be said that there was no significant difference between the averages. For the parallel samples, the breakage took a while to happen, close to 15 minutes, and the sample presented considerable deformation before breaking. SmartAgain® deformed more than PP and also presented lower E-modulus and higher maximum strain. This ductile behavior can be beneficial for its application in the printing of pump tracks.



**Figure 7** - E-modulus results for SmartAgain®.

Bending test was also performed, in the same way as previously mentioned for polypropylene, with 1A SmartAgain® bars. The results can be seen in **Table 4**. It is possible to notice that both printing speeds led to similar results, and, after a Student t-test, it could be said that there was no significant difference between them. Regarding breakage and strain, different results were found: SmartAgain® samples never broke during the test and a considerably higher maximum strain was found, showing that the material behaved in a less brittle way, pointing out that SmartAgain® might be a good material for printing the pump tracks.

**Table 4** - Bending test results for SmartAgain® - E-modulus, maximum

Speed	E-mod (MPa)	$\sigma_{fm}$ (MPa)	$\epsilon_{fm}$ (MPa)	$\epsilon_{fb}$ (MPa)
40 mm/s	793.96	28.14	35.82	7.57
70 mm/s	820.85	28.39	37.31	7.35

Considering all results found for SmartAgain® it can be concluded that this material can be a good choice for printing the pump tracks, since it behaved in a more ductile way than glass fiber reinforced polypropylene. It is recommended to develop more tests, especially on a big scale, to have more data about printing on the production scale with SmartAgain®. As for polypropylene, it was also seen that SmartAgain® did not completely crystallize with the first deposition of material when printing the 4cm wall, leaving room for the crystals to form in the interlayers region.

## 4. Conclusions

The temperature profile changed when changing the printing speed. For polypropylene, slower printing resulted in higher temperatures for more layers, due to the optimized heat transfer between the nozzle and the sample. For SmartAgain faster printing presented a higher temperature profile, but some warping was noticed, making the sample move when printing and affecting the heat transfer.

The crystallization during printing was analyzed by plotting together the half-time crystallization curve and the temperature profile. For both materials, this curve did not intercept the temperature profile, not for faster nor for slower printing, suggesting that crystallization was not completed with the first deposition of material. Since it was still possible to crystallize, when a new layer is deposited there is a chance that post-crystallization will occur between the layers, improving the layer to layer adhesion.

For the mechanical tests, the chosen printing speed led to similar properties. Through Student t-test, it can be said that there was hardly any significant difference between the samples printed at 40 mm/s for the ones printed at 70 mm/s. Polypropylene and SmartAgain® behaved differently. SmartAgain® presented a more ductile behavior, a lower E-modulus and a higher maximum strain and it deformed more before breaking. These characteristics make it a good choice for the development of production scale tests in order to use it in the printing of pump tracks. Polypropylene reinforced with 20% glass fiber is not recommended for the desired application, since the attempt made to print 1A bars with it failed due to warping. The same problem will probably be seen in production-scale printing.

## 5. Recommendations

To further improve this project, production scale tests should be done. It would be important to see how printing big samples with SmartAgain® will occur and if any problem that was not seen when printing at lab-scale will be faced. It is also important to have data on the mechanical properties of these samples to confirm that the model developed by Vranken, 2021 [2] is suitable for different materials.

It can be interesting to better investigate how crystallization occurs, checking if the region between the layers is predominately amorphous or crystalline, through WAXD or SAXD. With this data, new samples can be printed and tested and their mechanical performance can be better understood. It would also be recommended to check how polypropylene crystallizes during the printing of the 4cm wall sample. Since it is not possible to get the entire half-time curve, just the first line of the sample could be printed and a DSC could be done, calculating, then, the crystallinity of the first deposition of material.

## 6. Acknowledgement

This project was supported by Chemelot Innovation and Learning Labs and the Dutch government, through the OpZuyd Circular Polymer Project. The support of Zuyd Hogeschool and Maastricht University is also gratefully acknowledged, as well as the Living Lab Biobased Program, which enables the exchange of Brazilian and Dutch students. The assistance of Tosca van Hooy, Lucienne Bouvrie and Chantalle Zwarthoed during project development and experimental work is highly appreciated.

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