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O 4.1

Operational large-scale 3D-printing of biopolymers

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Abstract
This report describes the large-scale 3D-printer being operational at Poly Products (Werkendam, The Netherlands) for printing biopolymers. It is a printer with FDM-technique where the polymer is applied by means of an extruder. From the deliverable D 2.1.1 it is known what are the points of attention for printing biopolymers with the large-scale 3D-printer. As proof that the 3D-printer is operational for processing of biopolymers (O 4.1), following tests were performed with biopolymers that are in use in the SeaBioComp-project: TPS (Thermoplastic Starch), TPS-NF (natural fibre reinforced TPS) and PLA (Poly Lactic Acid). The tests worked good and prototype fender profile parts could be printed with the biopolymers. This proves a TRL-level up to TRL-6. By printing a full-scale fender profile with TPS-NF a TRL-7 level is proven. In this report also the eco-efficiency of 3D-printing of biopolymers is evaluated. As compared with the traditional production of products, the 3D-printing of biopolymers has a large eco-efficiency because 1) no moulds are needed to make the product, 2) there is practically no production waste (e.g. no trimming losses), 3) a sustainable material is used (biopolymer) and 4) the product can be recycled after End-of-Life stadium.

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Introduction

Within the SeaBioComp-project a large-scale 3D-printer is to be made operational for the production of products made from biopolymers. This also comprises bio-based composites with natural fibre (NF) reinforcements. In October 2019 at Poly Products (Werkendam, The Netherlands) a large-scale 3D-printer has been installed that operates with FDM-technique (Fused Deposition Modelling), using a movable extruder for the deposition of the molten thermoplastic polymer compound.

In order to adapt this machine for processing with biopolymers, it has been investigated what adaptations are necessary. This study has been performed and has been described in the deliverable report D 2.1.1 of the SeaBioComp project (*Adaptations for processing of biopolymers in 3D-printing*, 29 November 2019, see www.seabiocomp.eu). The main conclusions of this study were the following.

When natural fibre reinforced biopolymers are processed the maximum extrusion temperature should not be higher than 170 °C in order to prevent degradation of the fibre material.

In case of bio-based polyesters, including PLA, it is important to verify with the supplier whether corrosive substances are to be expected during processing at specific temperatures. If there remain doubts about corrosive substances that may be formed, a pre-screening test is advised to be done as was developed by Centexbel. This test can also be used to determine if the corrosion observed is the result of the used biopolymer or a different polymer.

To minimize the risk of corrosion due to acidic by-products adequate pre-drying of the granulate should be done and processing temperatures should be limited according to instructions of the supplier or by the recommendations given in D 2.1.1.

Because there is at this stage of the SeaBioComp project no evidence that corrosive substances can not be prevented, it is advised not to change the extruder parts of the 3D-printer from steel to stainless steel. The reason for this is that stainless steel is much more sensitive for abrasion (wear) and the 3D-printer is to used also for other projects than SeaBioComp where abrasive compounds can be used (e.g. compounds with glass fibres).

In this report, Section 1 describes the 3D-printer for FDM that is used for the SeaBioComp-project. Sections 2 describes the tests on this printer with the biopolymers TPS and PLA. In Section 3 the eco-efficiency of the 3D-printer using biopolymers is evaluated by making a comparison with a traditional way of the manufacturing of the composite products. Finally, conclusions are given in the last section.

All reports and deliverables that are referred to in this document are available on the SeaBioComp-website (www.seabiocomp.eu) or will be made available shortly.

1 Description of the 3D-printer and printing process

The FDM-printer that is used for the SeaBioComp project has been built by CEAD in Delft (The Netherlands) and is installed at Poly Products in Werkendam (The Netherlands) in October 2019. The machine is depicted in the photo in Figure 1. The machine can print very large products with dimensions up to (LxWxH) 4 x 2 x 1.5 m, which makes it a very interesting technique for printing biocomposite products for marine applications as very little assembly is required after production of complex geometries.

Figure 1 FDM-printer of Poly Products

Main components of the machine are :

- Structural frame for the support of the x-y-displacement system
- X-Y-displacement system
- Extruder with integrated melt-pump
- Built plate that can be moved in z-direction
- Isolated casing
- Pre-drying installation (seperate drying set-up that can feed the extruder of the printer)
- System control

The process of 3D-printing starts with the drying of the polymer granulate. For most polymers the drying is an essential step to prevent polymer degradation and, in case of thermoplastic polyesters the formation of corrosive substances.

After drying the granulate is fed into the extruder and is plasticized by the heated zones in the extruder in combination with the heating by the shear of the viscous polymer. On the control screen the temperature settings and measured temperatures at different locations in the extruder, in the melt pump and in the nozzle are displayed, see photo in Figure 2.

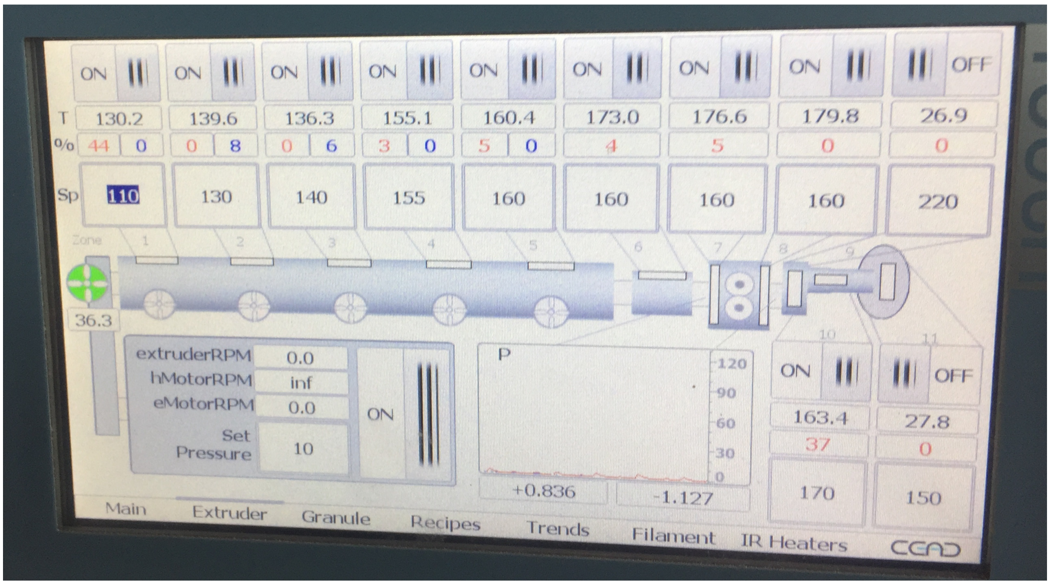

Figure 2 Display of temperatures in extruder, melt-pump and nozzle.

From the nozzle, the molten polymer is deposited on the previous layers. This is done in a space that is isolated for maintaining a constant temperature, see Photo 3 (left). An IR-image (made by IMT Lille-Douai) shows the heat distribution of the nozzle and deposited material, see photo in Figure 3 (right).

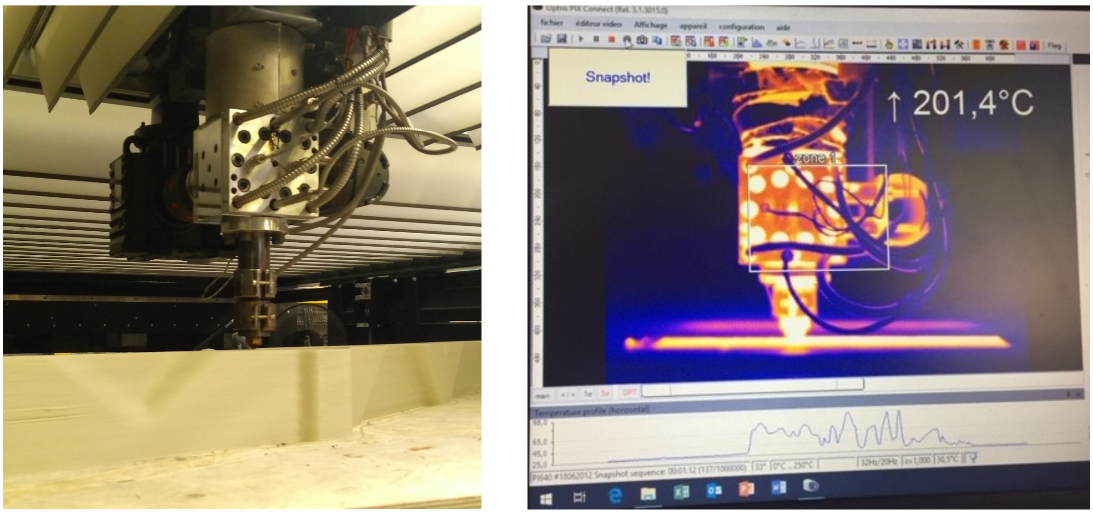

Figure 3 Printing in action (left) and IR-image of temperature distribution (right).

In order to characterize the printing process, parameters are introduced. These parameters are the diameter of the circular opening of the nozzle where the polymer comes out (d), the width (W) and the thickness (t) of the layer that is formed and the horizontal speed (v) of the nozzle. With these parameters the formation of the layer by the polymer that comes out of the nozzle (see photo in Figure 4) can be described.

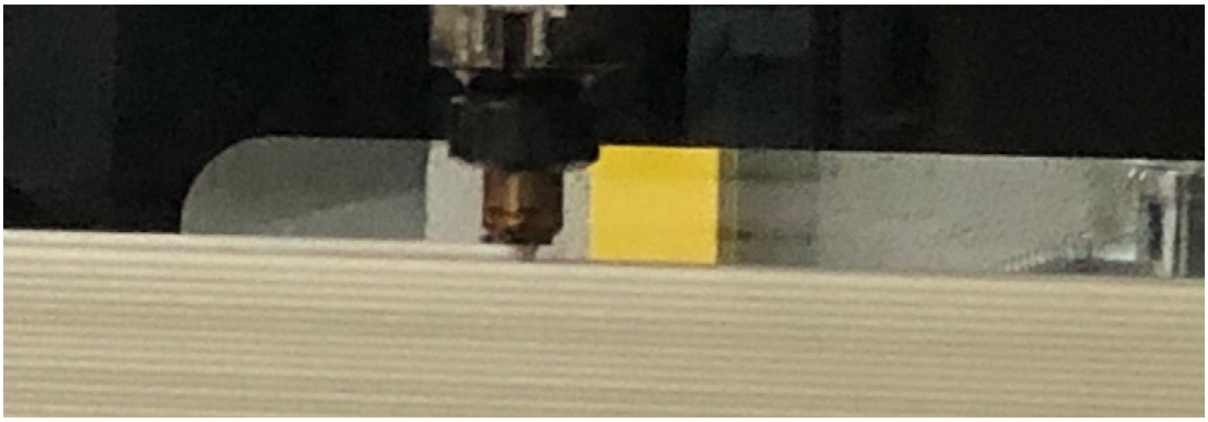

Figure 4 Detail of the formation of the layer by the nozzle.

The extruder output (Φ in kg/hr) is related to the parameters in the following manner :

$$\Phi = \rho \cdot W \cdot t \cdot v \qquad (1)$$

In which :

Φ	=	extruder output	in kg/hr
ρ	=	density of the polymer compound	in kg/m^3
W	=	width of the layer	in m
t	=	thicknes of the layer	in m
v	=	horizontal speed of the nozzle	in m/hr

In principle the layer dimensions are independent from the diameter of the opening of the nozzle. However, in practise the following empirical limits are found :

$$d < W < 2d \qquad (2)$$

As an example the printing of a polymer with a density of 1300 kg/m^3 is considered with a horizontal speed of 300 m/hr and resulting in layers with a width of 7 mm and a thickness of 2 mm. The extruder output can then be calculated :

$$\Phi = \rho \cdot W \cdot t \cdot v = 1300 \cdot 7 \cdot 10^{-3} \cdot 2 \cdot 10^{-3} \cdot 300 = 5.46 \text{ kg/hr}$$

2 Tests with TPS, PLA and TPS-NF

For the evaluation of the suitability of the 3D-printer for making products of biopolymer products in the SeaBioComp-project, two biopolymers are selected that are relevant in view of the other developments in the project. These are Thermoplastic Starch (TPS) and Poly Lactic Acid (PLA). More specifically the following product types are selected :

TPS : Solanyl C8201 (Supplier : Rodenburg Plastics)
PLA : Purapol L130 (Supplier : Corbion – formerly PURAC)

The characteristics of these polymers are given in Table 1.

Property (Data sheets)	Symbol	Unit	Solanyl C8201	Purapol L130
E-modulus	E	GPa	1.7	3.5
Tensile strength	σ	MPa	30	50
Strain at yield	ε	%	5	5
Density	ρ	kg/m^3	1300	1240
Glass transition temp.	T_g	°C	57	55 – 60
Melt temperature	T_m	°C	140 – 160	175

Table 1 Characteristics of Solanyl C8201 and Purapol L130.

From the data it is clear that for the selected product types PLA is mechanically stiffer and stronger than TPS. However, the glass transition temperature and the melting temperature are in the same range. Both are known for their biodegradability and compostability under industrial composting conditions (high temperatures and humidities).

From the deliverable report D 2.2.1 (Report on the base biopolymer formulations for large scale additive manufacturing, May 2020) the mechanical strength in the print direction (indicated with 0°) of the selected biopolymers that were 3D-printed are given in Table 2.

Property (printed, 0°)	Symbol	Unit	Solanyl C8201	Purapol L130
E-modulus	E	GPa	0.6	1.8
Tensile strength	σ	MPa	13	38
Maximum strain	ε	%	2.4	2.5

Table 2 Properties (0°) of 3D-printed Solanyl C8201 and Purapol L130.

It must be remarked that the strength perpendicular to the print direction (90° direction) is generally much lower than the strength in print direction (0° direction) as a result of low interlayer strength. In case of Solanyl C8201 strengths in 90° direction were found to be typically 20% or lower than the strength in 0° direction.

In the following the printing of prototype fender profiles with these biopolymers is described. The prototype profiles were printed with the profile axis vertically and with a profile length of 300 mm.

Printing of TPS Fender profile

At the 3D-printer of Poly Products, products as depicted in Figure 5 were printed using Solanyl C8201 of Rodenburg Plastics. A nozzle opening of 4 mm was used to print a product with a wall thickness of 6.5 mm. As a general rule for the outside corners of a printed product a radius of about 2 times the layer width is chosen. In this product the outside radius is set to 12 mm.

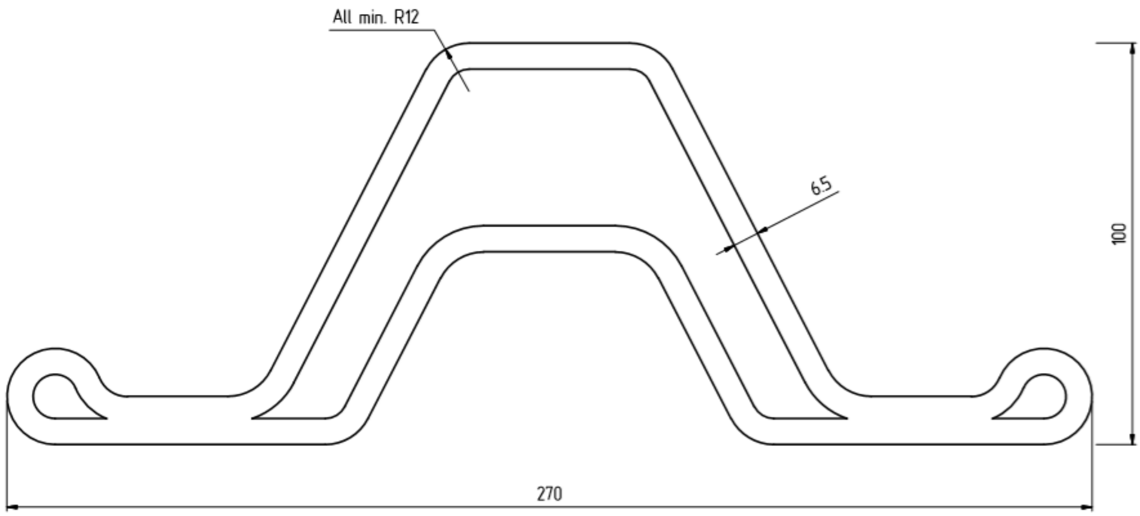

Figure 5 Fender profile, initial design for 3D-printing in TPS

Initial tests showed that an outer radius in the corners of R = 12 mm gave too much heat remaining so that locally the product shape is deformed during the printing process. Obviously,the radius around a closed area should be chosen larger. Therefore, in the closed corner areas the radius is set to four times the layer width :

$$\mathbf{R_{closed\ corner} = 4\ W = 24\ mm}$$

When the machine settings were further optimised, four prototype products with a height of 300 mm were printed in one print run. The printing and the end result is given in de photo's in Figure 6.

Figure 6 Printing of four prototype fender scale products and cross-section.

During printing the following parameters were used, see Table 3.

Parameter	Symbol	Unit	Value
Temperature barrel extruder	T_b	°C	160
Temperature nozzle	T_n	°C	170
Nozzle diameter (opening)	d	mm	4.0
Layer thickness	t	mm	1.5
Layer width (wall-thickness)	W	mm	6.5
Printing speed	v	m/min	2.0
		m/hr	120
Extruder output (*)	Φ	kg/hr	1.52

Table 3 Printing parameters of prototype fender profiles with TPS.

The extruder output (*) is calculated from the other parameters, using the specified density of the polymer of 1300 kg/m^3 with formula 1 :

$$\Phi = \rho \cdot W \cdot t \cdot v = 1300 \cdot 6.5 \cdot 10^{-3} \cdot 1.5 \cdot 10^{-3} \cdot 120 = 1.52 \text{ kg/hr}$$

In cooperation with De Klerk Waterbouw (observer partner in the SeaBioComp-project), an improved design for a fender profile has been developed for a demonstrator product. The profile width is 400 mm, the profile height is 300 mm and the wall-thickness is 10 mm. For testing, three profile parts of 300 mm length of this improved design were printed and tested mechanically by De Klerk Waterbouw (see SeaBioComp report : *Development of 3D-printed biopolymer fenders – Report 1 – Background, first designs and tests*, March 2020). These parts were printed of a reference material (rPETG-GF30 *) with a wall-thickness of 10 mm. In Figure 7, a photo is given of a profile part.

Figure 7 Improved fender profile design, printed in rPETG-GF30.

*) rPETG-GF : recycled Poly Ethylene Terephtalate Glycol-modified, 30% Glass Fibre reinforced

The same, thick-walled fender profile was also printed with TPS. This worked well, although the products showed more surface irregularities, see the photo in Figure 8. This will be a matter of process optimisation to improve the surface quality.

Figure 8 Improved fender profile (10 mm wall-thickness) printed in TPS.

Printing of PLA Fender profile

From the tests with De Klerk Waterbouw the design of the fender profile is further optimised. The side-walls are made more curved so that it gives more flexibility. The central hole is optional for filling with energy-absorbing elements, e.g. rubber. This has resulted in the following design, see Figure 9.

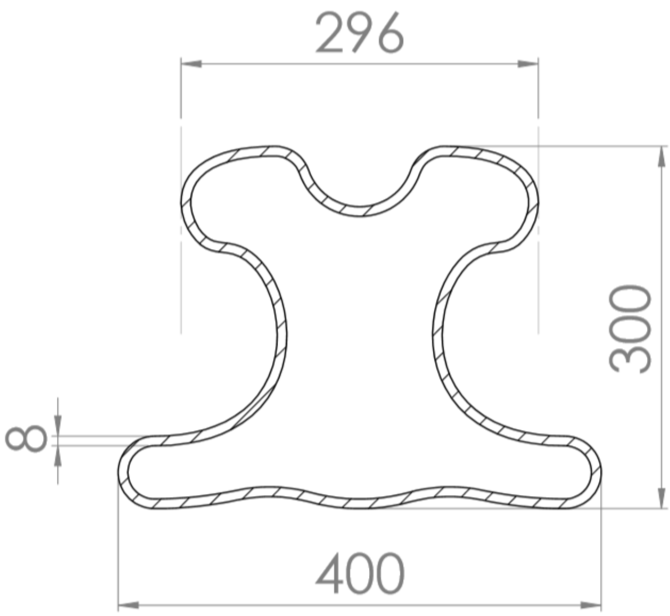

Figure 9 Further improved fender profile design (3).

Of this design a profile part is printed with PLA. During printing the following parameters were used, see Table 4.

Parameter	Symbol	Unit	Value
Temperature barrel extruder	T_b	°C	200
Temperature nozzle	T_n	°C	180
Nozzle diameter (opening)	d	mm	6.0
Layer thickness	t	mm	2.0
Layer width (wall-thickness)	W	mm	11.5
Printing speed	v	m/min	2.0
		m/hr	120
Extruder output (*)	Φ	kg/hr	3.42

Table 4 Printing parameters of prototype fender profiles with PLA.

The extruder output (*) is calculated from the other parameters, using the specified density of the polymer of 1240 kg/m^3 with the following formula :

$$\mathbf{\Phi = \rho \cdot W \cdot t \cdot v = 1240 \cdot 11.5 \cdot 10^{-3} \cdot 2.0 \cdot 10^{-3} \cdot 120 = 3.42\ kg/hr}$$

The resulting profile that was printed with PLA is given in the photo in Figure 10. Although the printing went well, surface irregularities occurred, possibly because of a too low viscosity of the molten polymer. This will also be a matter of process optimisation for obtaining a better quality.

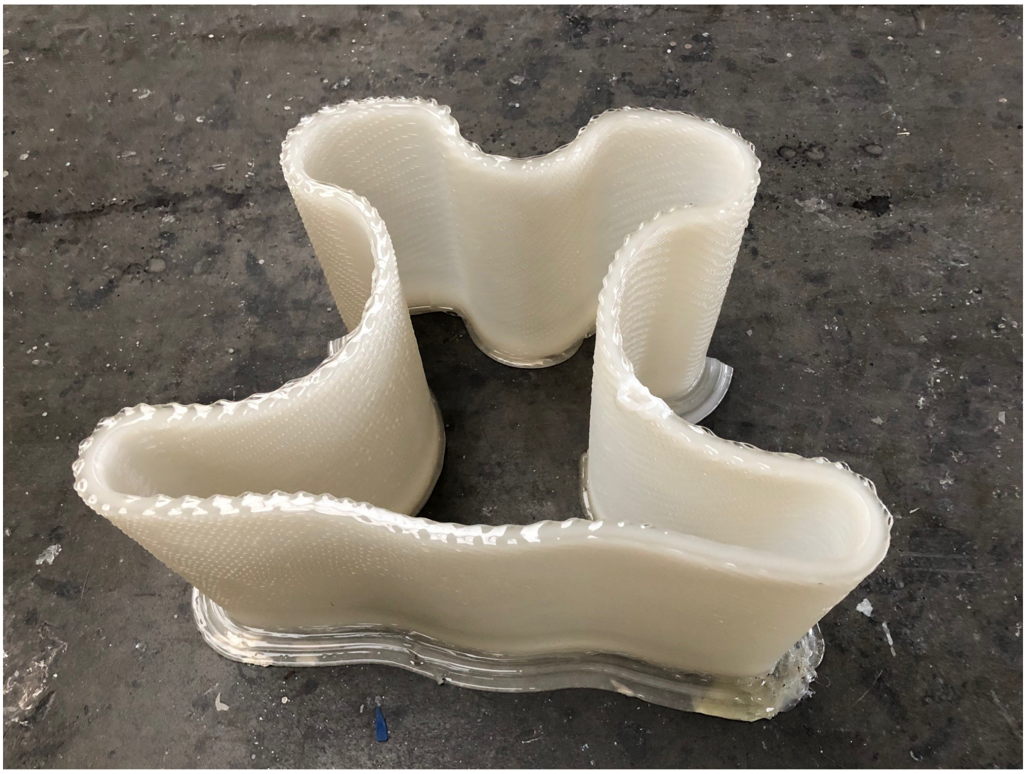

Figure 10 Further improved fender profile (3) printed with PLA.

As a final test for the 3D-printer being operational for the SeaBioComp project, a natural fibre (NF) reinforced TPS-compound has been used to print a full-scale fender profile. The further improved fender profile (3) has been used as a basis for the following design of a semi-sized demonstrator that is to be tested in a real situation by De Klerk Waterbouw. The design consists of the profile with an effective length of 1,5 meter, with one side closed to form a bottom. At this bottom side also a joggle is formed in the wall so that this side can fit in the top of a underlying fender profile. The profiles are mounted vertically on a quay wall. Figure 11 shows a piece of such a fender profile.

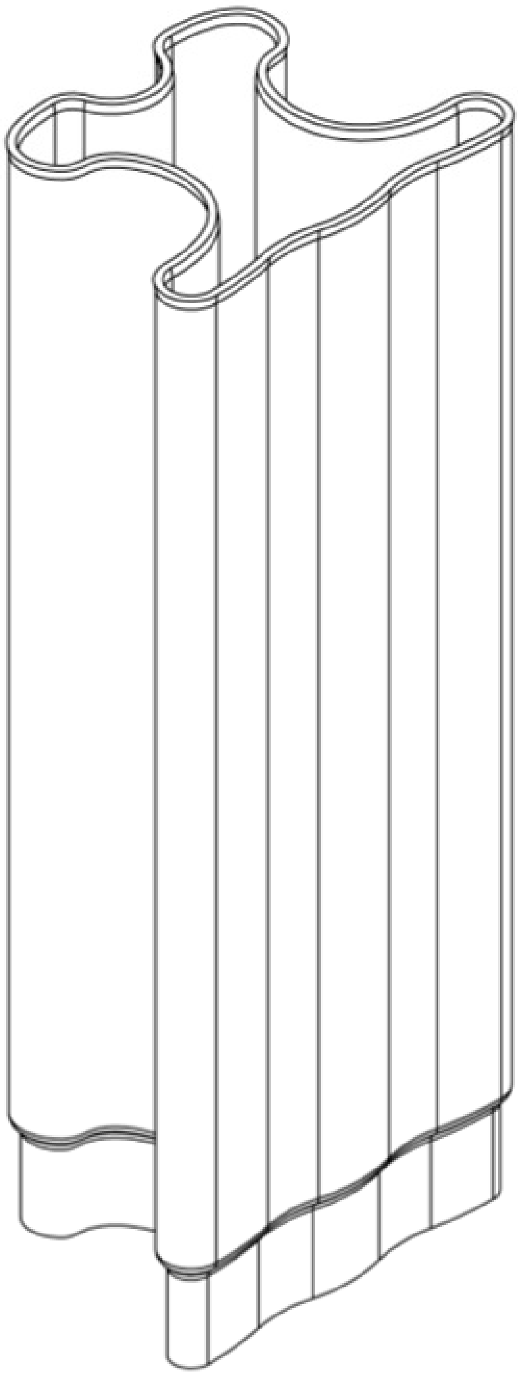

Figure 11 Fender profile for vertical mounting on a quay wall.

At the lower side of the fender profile a closed bottom is formed, see the cross-section in Figure 12. This closed bottom offers the possibility that open core of the profile is filled with other materials. It is an subject for further investigation whether the filling of this core, e.g. with rubber pieces from old car tyres may help for energy absorption.

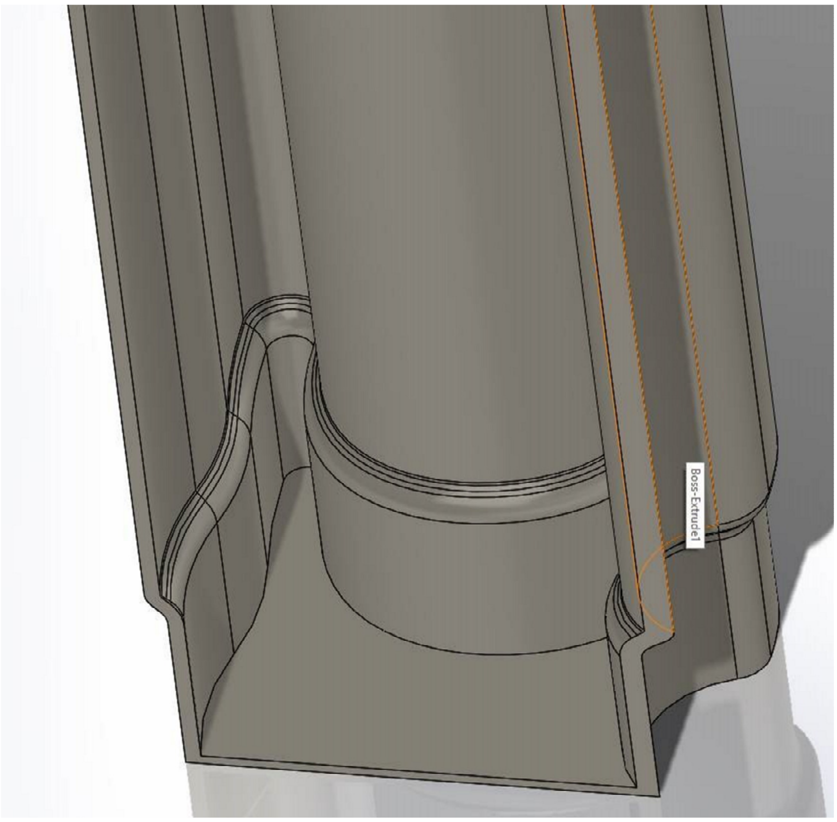

Figure 12 Detail of the closed bottom of the fender profile.

The TPS-NF compound that was used to print such profiles is the TPS Solanyl C8201 of Rodenburg Plastics that is filled with 20% (by weight) hemp fibres. First a thin-walled square tube is printed of this material to determine optimum printing parameters and for making test specimens for the determination of mechanical properties (not within the scope of O 4.1), see Figure 13. Printing parameters are given in Table 5.

Parameter	Symbol	Unit	Value
Temperature barrel extruder	T_b	°C	165
Temperature nozzle	T_n	°C	160
Nozzle diameter (opening)	d	mm	4.0
Layer thickness	t	mm	1.2
Layer width (wall-thickness)	W	mm	5.5 (installed) 6.17 (measured)
Printing speed	v	m/min	2.1
		m/hr	126
Extruder output (*)	Φ	kg/hr	1.52

Table 5 Printing parameters of thin-walled square tube with TPS-NF

The extruder output (*) is calculated from the other parameters, using the measured density of the polymer of 1100 kg/m^3 (**) with formula 1 :

$$\mathbf{\Phi = \rho \cdot W \cdot t \cdot v = 1100 \cdot 6.17 \cdot 10^{-3} \cdot 1.2 \cdot 10^{-3} \cdot 126 = 1.03\ kg/hr}$$

The density of the compound (**) could be calculated from the volume of the thin-walled square tube and the weight. The 205 mm heigh tube had a volume of 2.45 liter and weighed 2.691 kg from which a density is calculated of 1100 kg/m^3. It is important to mention that the compound showed substantial die-swell at the exit of the nozzle. This is reflected in a layer width that is much higher (6.17 mm measured) than is installed (5.5 mm).

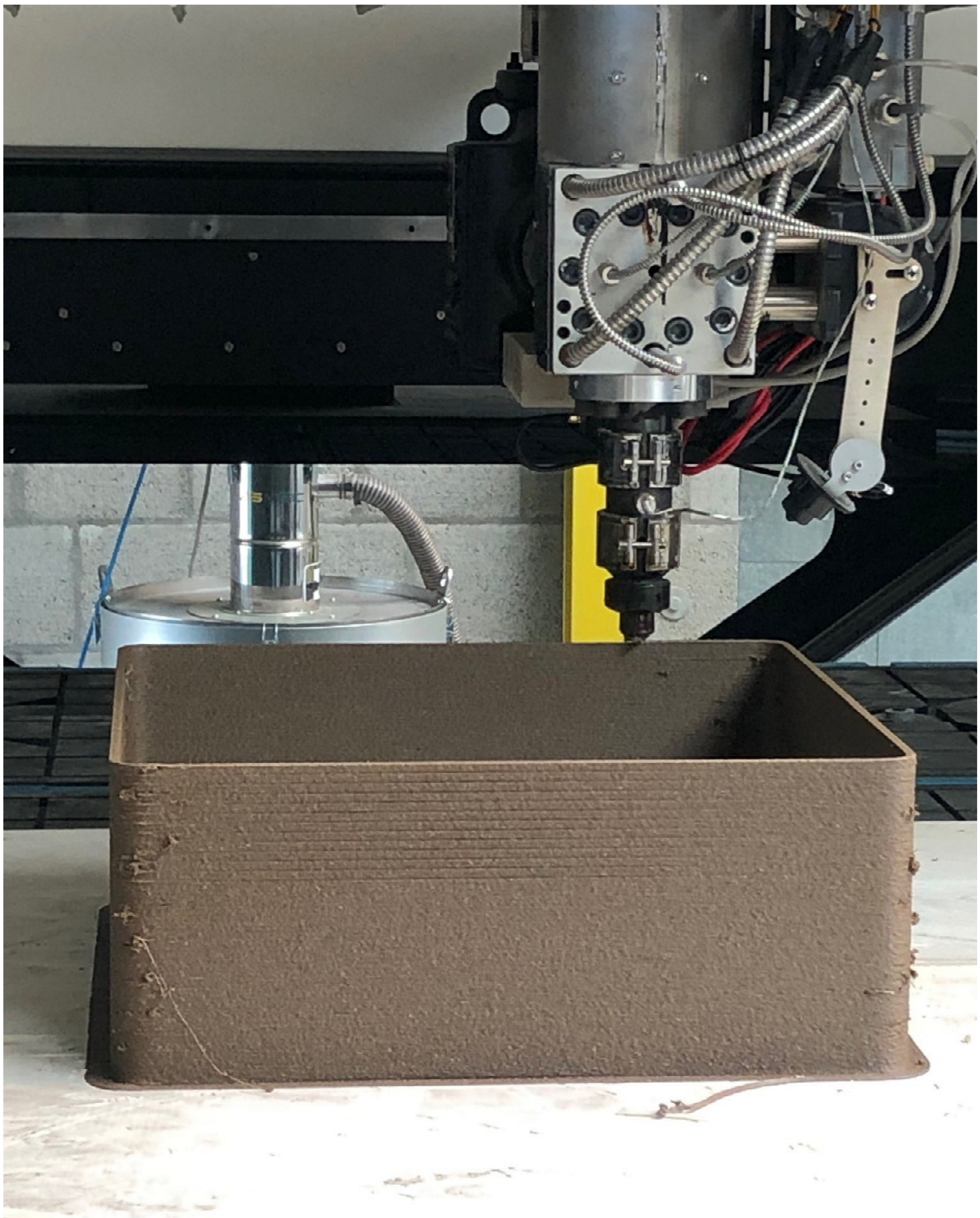

Figure 13 Printing of thin-walled square tube of TPS-NF

For printing the full-scale fender profiles with TPS-NF a higher layer thickness and layer width are installed. Printing parameters are given in Table 6.

Parameter	Symbol	Unit	Value
Temperature barrel extruder	T_b	°C	165
Temperature nozzle	T_n	°C	160
Nozzle diameter (opening)	d	mm	8.0
Layer thickness	t	mm	2.4
Layer width (wall-thickness)	W	mm	11.0 (installed) 13.33 (measured)
Printing speed	v	m/min	2.3
		m/hr	138
Extruder output (*)	Φ	kg/hr	4.86

Table 5 Printing parameters of prototype fender profiles with TPS-NF.

The extruder output (*) is calculated from the other parameters, using the measured density of the polymer of 1300 kg/m^3 with formula 1 :

$$\Phi = \rho \cdot W \cdot t \cdot v = 1100 \cdot 13.33 \cdot 10^{-3} \cdot 2.4 \cdot 10^{-3} \cdot 138 = 4.86 \text{ kg/hr}$$

Again a substantial die-swell is observed, resulting in a higher layer-width (13.33 mm) and that was installed (11.0 mm). Two prototype profiles have been printed with a height of 310 mm. The resulting profile is shown in Figure 14, both from the side and from the bottom.

Figure 14 Printed prototype fender profile made of TPS-NF.

Because of the die-swell the profile parts did not fit into each other over the full length of the joggle. This is something for further optimization of the design to take into consideration the possible occurrence of die-swell. The fitting of the two profile parts in each other is shown in Figure 14.

Figure 14 Fitting of two prototype fender profiles of TPS-NF.

3 Eco-efficiency and TRL-levels of large-scale printing of biopolymers

The eco-efficiency of large-scale printing of biopolymers is obvious. There are several aspects that are beneficial when sustainability and eco-friendlyness are considered when the large-scale printing of biopolymers is compared with the traditional methods of producing composite products :

- No models or moulds needed for the product shape
- Practically no spillage of material during production
- Use of bio-based materials
- At End-of-Life (or End-of-Use) the product can be recycled due to the use of thermoplastic polymers

Because a comprehensive and general investigation of the eco-efficiency of 3D-printing of biopolymers is beyond the scope of this report, a reference product is selected to make a comparison between production using large-scale printing of a biopolymer and traditional composite production. As a reference product a double-curved shell is selected with the following characteristics :

Net product surface :	6 m^2
Wall-thickness :	6 mm
Outer surface :	top-coated
Number of products to be produced :	10

The production methods that are compared are given in Table 6.

	Traditional composite production GRP (thermoset)	Large-scale 3D-printing NF-reinforced biopolymer
Model	YES	-
Production mould	YES	-
Cost of model and mould	€ 9000	-
Lead time model and mould	6 weeks	-
Origin raw materials	Fossil-based, not sustainable	Bio-based, renewable
Compound density	1800 kg/m^3	1100 kg/m^3
Production spillage	10 %	1 %
Production time of 1 product	1 working day	5 hours
Labour time	13 hours	5 hours
Trimming spillage	10 %	1 %
Product weight	65 kg	40 kg
Product cost (*)	€ 1250	€ 750
Top-coating	YES	YES
End-of-Life / End-of-Use	Not recyclable	Recyclable (circular)

*) Product cost includes material, labour, machine-use, energy, production space and overhead, but is exclusive of sales margin.

Table 6 Comparison GRP composite production and 3D-printing with NF-biopolymer

From this comparison it is clear that the eco-efficiency with large-scale 3D-printing with NF-reinforced biopolymer is much higher than it is the case with traditional composite production. The use of additive manufacturing could result in as much as 40% reduction of product cost during a production run (i.e. optimized product with available moulds).

This does not take into account the one-time large investment that is to be made upon purchasing of the additive manufacturing equipment compared to the more frequent investments in moulds required upon even minor modification to the product design. Finally, careful product design and print paths could make it possible to print multiple iterations of the same product in parallel, while multiple moulds are required in traditional composite fabrication.

TRL-levels are used to determine the Technical Readiness Levels of a technology. The levels are defined generally as follows :

TRL 1 – Basic principles observed

TRL 2 – Technology concept formulated

TRL 3 – Experimental proof of concept

TRL 4 – Technology validated in lab

TRL 5 – Technology validated in relevant environment

(industrially relevant environment in the case of key enabling technologies)

TRL 6 – Technology demonstrated in relevant environment

(industrially relevant environment in the case of key enabling technologies)

TRL 7 – System prototype demonstration in operational environment

TRL 8 – System complete and qualified

TRL 9 – Actual system proven in operational environment

(competitive manufacturing in the case of key enabling technologies; or in space)

The TRL-levels in de SeaBioComp-project for 3D-printing of biopolymer products are shown to be reached in the following list:

TRL 1 and 2
Basic principles of 3D-printing of biopolymers concept formulation are described in the deliverable report D 2.1.1.

TRL 3 and 4
Experimental proof of concept on lab-scale and small-scale optimization of fabrication conditions has been performed by Centexbel by their 3D-printing of PLA-compounds on the 3D-printer that works on PLA-granulate.

TRL 5
Fabrication of small samples for mechanical testing has been done by Poly Products for printed TPS (testing done by the University of Portsmouth) and by Centexbel for printed PLA. The results of these tests are given the present report.

TRL 6
Fabrication of pieces of fender profile structures both in TPS and PLA are described in this report.

TRL 7
Fabrication of full-scale fender profiles printed in TPS-NF are described in this report.

Conclusions

The large-scale 3D-printer that is installed at Poly Products is suitable for the processing of biopolymers. By printing several fender profile parts with Thermoplastic Starch (TPS), with Poly Lactic Acid (PLA) and natural fibre reinforced TPS it is shown that the machine is suitable for printing demonstrator products with biopolymer for the SeaBioComp project.

Although the printer works for printing with TPS, TPS-NF and PLA there are points of attention for process optimisation. The low strength perpendicular to the printing direction should be improved, specially for TPS. Moreover, for printing products with closed areas or sharp curvatures methods must be developed to remove the heat to prevent product distortion. Possibly local ventilation may help for this. Finally, the surface quality of the printed products with TPS and PLA must be improved by optimisation of temperature settings in the process. Also the occurrence of die-swell must be taken into account when designing with 3D-printed biopolymers. This phenomenon has been observed specially with the TPS-NF-compound.

With the products described in this report an extruder through-put up to 5 kg/hour has been used. When further optimizations are made in product design and process parameters, a through-put is expected to be achievable of 10 to 15 kg/hour.

When the eco-efficiency is considered of large-scale 3D-printing of biopolymers for the manufacturing of products it is clear that this is much better than the traditional method of composite products using thermosetting fossil-based materials. Important to note is that Additive Manufacturing allowed the rapid prototyping of 4 sequential fender profiles, including a full-scale version, already in the first year of the SeaBioComp-project.

A TRL-level up to TRL-6 is proven with full-scale fender profile parts that have a detailing that is required for the use in practise.