INnovative fIshing Gear for Ocean

T2.1.2 Semi-finished products developed at laboratory scale

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EUROPEAN UNION

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Summary

I. Introduction

Within the framework of WP2 of the INdIGO project two biodegradable materials are being developed, one for use in a fishing net, one for a mussel aquaculture net. This deliverable T2.1.2 of this activity includes formulations produced by NaturePlast and semi-finished products, monofilament and multifilament, developed at the laboratory scale by UBS from plastic formulations. This technical report describes the different processing steps of the different formulations. Many formulations were tested to assess the mechanical behaviour and processability of various candidate polymers and additives:

- For aquaculture net: more than 30 formulations.
- For fishing net: more than 45 formulations.

This report details the various tests carried out on pellets of compounds and injected test bars, in order to characterize the materials and to improve formulations: mechanical tests (tensile test at break, Young's modulus, flexural modulus, cyclic test, impact test), rheological test (Melt Flow Index: MFI), density…

Moreover, the plastic granules were processed in an extruder to obtain both multifilament and monofilament. Depending on the type of semi-finished product (mono or multifilament), the processing equipment is not the same. The machines used, as well as the processing properties such as temperatures, screw speed, applied drawing ratio were defined so that the tests can be reproduced later. All the characterization tests on filament prototype are also presented in this report: mechanical strength, strain before filament rupture... These are all essential parameters that are of great interest to target groups such as fisheries and aquaculture professionals. These filaments will then be used in Activity 2 by FILT to test their spinning ability on net-making machine, and exchanges will be planned between partners to ensure that the filaments will be easily adapted during the manufacturing process.

II. Development strategy for laboratory-scale semi-finished products

Activity 1 of work package 2 is central to ensuring the development of semi-finished products that meet the specifications and is also an essential stage in the success of the INdIGO project. By means of the diagram presented in figure 1 below, the partnership wished to clearly present the development strategy for semi-finished products at both laboratory and semi-industrial scale. The partners involved in this deliverable are therefore NaturePlast, the University of Southern Brittany (UBS) via its ComposiTIC technical platform, IRMA and Filt to provide its expertise on the filaments developed.

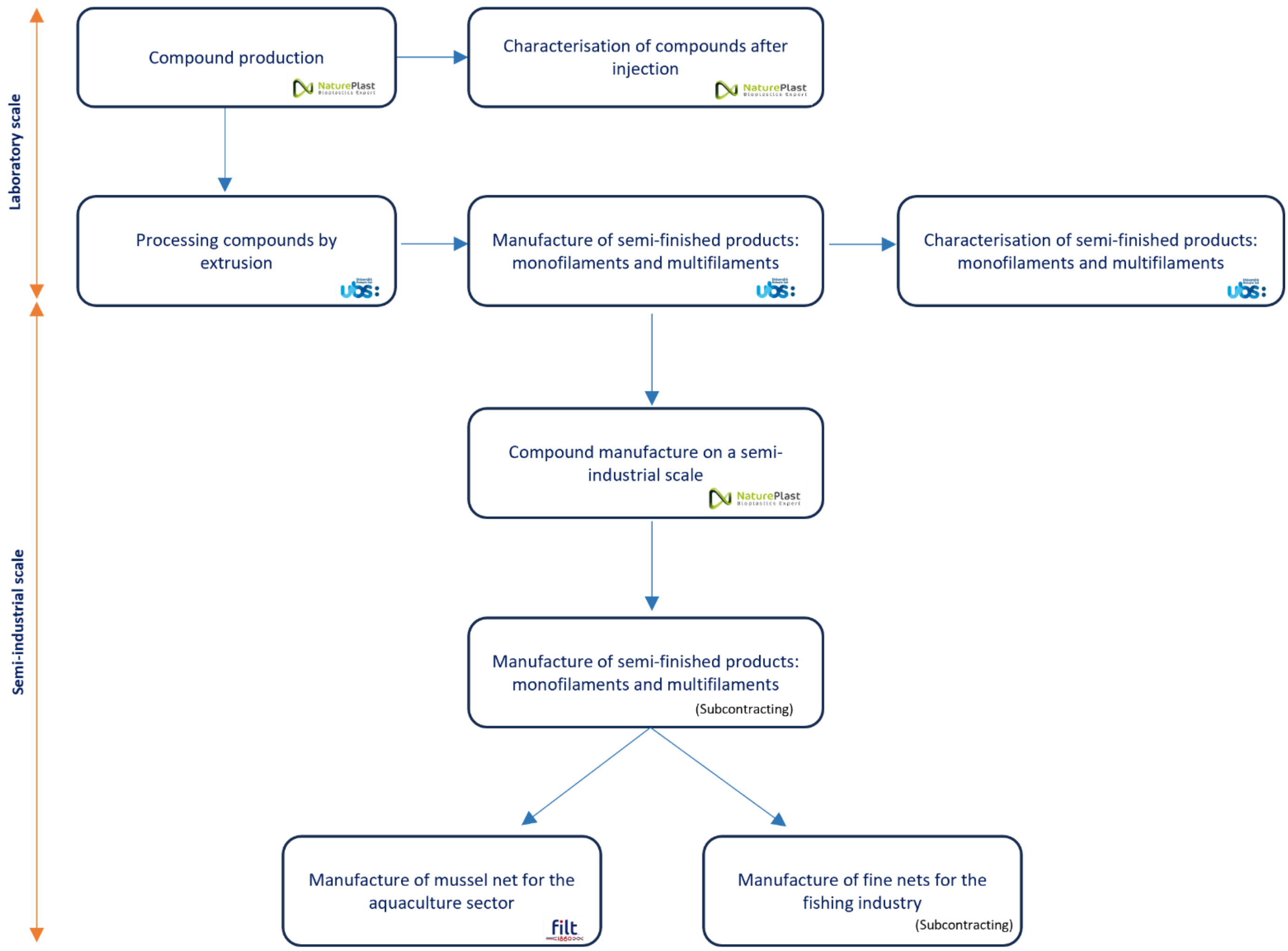


Figure 1: Development strategy for semi-finished products at lab and semi-industrial scale

The descriptions presented in this report only concern the first part of the scheme, concerning laboratory-scale development.

III. Choice of formulations

Target properties for each application are defined in the deliverable T1.2.1-Specificiations. Blends were defined by UBS/IRMA/NaturePlast based on this document.

Polymer candidates were selected based on various specificities:

- Rheological properties (specific requirements of fluidity defined by the equipment used for filament production).
- Mechanical properties (specific requirements of tensile strength, elasticity, etc defined by the targeted properties of final nets).
- Balance between effective biodegradation abilities and required sustainability.

Various types of additives were tested to increase one or several of the three property categories detailed above.

The list of the blend studied within the project is added in the confidential version of this deliverable.

The equipment used to produce the formulations is shown below.

1. Extrusion

Extrusion at lab scale was performed by **BiopolyNov** (Extruder 21 mm) whereas extrusion at semi-industrial scale was performed by **NaturePlast** (Extruder 27 mm).

a. Extruder 21 mm

In order to prepare the various blends at lab scale, a TSA FSCM 21-50 twin-screw co-rotative extruder, with a L/D ratio of 50 and five heating zones (four dedicated to the barrel, one to the die), is used (Figure 2). Two volumetric feeders are available for the various components incorporation inside the barrel as well as a liquid pump. Surrounding devices available also consist in a water-cooling bath and a pelletizer.

The lateral volumetric feeder can be moved along the barrel to choose the introduction zone of the second component. Moreover, several degasification zones can be opened if needed.

Figure 2: Twin-screw co-rotative extruder

b. Extruder 27 mm

A TSA co-rotative twin-screw extruder with a 27 mm diameter and a L/D ratio of 50, model TSA TT27-50 is used. The extruder is equipped with two gravimetric feeders Schenck Proflex C500, one as the main feed, the other via a side feed as well as a liquid pump (Figure 3). The introduction area of the second gravimetric feeder is adjustable. The two to six-hole strand die is followed by a water-cooling tank to cool the strands and convey them to the pelletizer.

Figure 3: Twin-screw co-rotative extruder TSA FSCM 27-50

The detail of the process parameters used to produce the various blends is added in the confidential version of this deliverable.

IV. Formulation characterisation

The first stage consists of manufacturing the compounds, NaturePlast was also responsible for characterising the various formulations, using conventional characterisation techniques after injection of the test specimen.

1. Injection

Injection was performed by **BiopolyNov**.

To perform mechanical tests, the blends have been injected as:

- dumbbells (specimen type 1A defined in EN ISO 527),
- simple bars (specimen 1 defined in EN ISO 179, L=80 mm, W=10 mm, T=4 mm).

Injection is performed using an injection molding equipment, model KM80-22 from Krauss Maffei (Figure 4).

Figure 4: Injection molding equipment

The detail of the process parameters used to produce the various injected samples is added in the confidential version of this deliverable.

2. Characterisation tests

Tests were performed by **BiopolyNov** except for accelerated ageing which was performed by **NaturePlast**.

a. Tensile test, flexural test, cyclic tensile test

Before testing, the dumbbell specimens are conditioned at least three days at 23°C and 50% RH.

The equipment used is a tensile bench, model 3367 from INSTRON, and is presented on Figure 5.

Figure 5: Tensile bench INSTRON 3367

For the mechanical properties at break, measurements are carried out following standard NF EN ISO 527. The testing speed is set at 50 mm.min^{-1}. Two cells can be used according to the level of load:

capacity 1 kN or 30 kN. Strain is measured by recording the displacement of the perpendicular bar of the tensile test equipment.

For Young's modulus, measurements are carried out following standard NF EN ISO 527. In particular, the testing speed is set at 1 $mm.min^{-1}$, and modulus is defined as the slope of the stress-strain curve between 0,05 and 0,25% strain. Cell load capacity is 1 kN. Strain is measured using a contact extensometer.

To determine the flexural modulus, the bench is equipped with a cell load capacity of 1 kN. Measurements are carried out following standard NF EN ISO 528. The measurement is carried out at 2 $mm.min^{-1}$.

Concerning cyclic tensile tests, the tests are controlled by imposing given load (not deformation). Two different types of stress profiles are defined (triangular and rectangular) on Figure 6:

- 1 : Loading phase
- 2: Constant load plateau (to assess deformation)
- 3: Cyclic stress

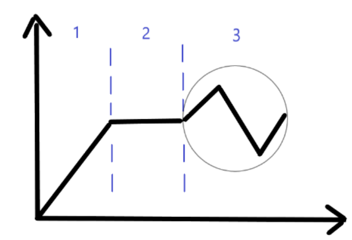
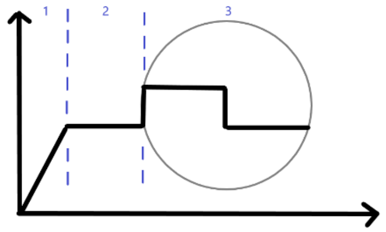
Triangular stress	Rectangular stress
	
Detailed parameters in confidential deliverable	*Detailed parameters in confidential deliverable*
Outputs: - Maximum/minimum strain during phase 2 - Maximum/minimum strain after specific number of cycles	Outputs: - Maximum/minimum strain during phase 2 - Maximum/minimum strain after specific number of cycles

Figure 6: The two types of cyclic solicitations

One of the aims of these fatigue tests is to simulate the stresses imposed on nets during their use phase:

- Fine nets: dynamic stresses to simulate the phases of use (launching into the water, subsequent reassembly on the boat, storage, etc.)
- Mussel nets: static stresses plus occasional overloads (weight due to shellfish growth, effects of tide and wind, etc.).

b. Charpy impact strength (unnotched)

Before testing, the test pieces are conditioned for a minimum of 3 days at 23°C and 50% RH. The tests are carried out on a CEAST Pendulum Impactor II device (Figure 7). The test pieces tested are bars of standardized dimensions (type 1 bar). The hammer used is a 2 or 15 Joule hammer, depending on the formulation.

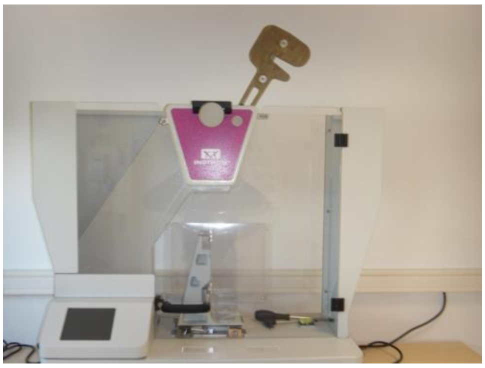


Figure 7: Impact pendulum Impactor II

c. Rheological properties

Before testing, all samples are dried in an oven at 90°C during at least 4 hours. This method enables to determine Melt Flow Index (MFI). The equipment is a Modular Melt Flow Tester from CEAST (Figure 8).

Figure 8: Modular Melt Flow Tester

Measurements are carried out according to standard NF EN ISO 1133. The oven is filled with pellets, and heated up to the desired temperature without load during 300s. A 2,16 kg load is applied and samples are cut at a regular time interval. Extrudates are then weighed to determine the Melt Flow Index, in g/10 min.

d. Density

Before testing, pellets are conditioned at least three days at 23°C and 50% RH. The equipment used is a precision scale type ALS/PLS 01, with density determination kit (Figure 9).

Figure 9: Density determination kit

Measurements are carried out according to standard NF EN ISO 1183 (immersion method). Liquid used is distilled water. Pellets are weighed in ambient air, then they are weighed after immersion in liquid with known density. Tests are carried out on pellets obtained after extrusion process.

e. Accelerated ageing

The accelerated aging chamber used for the tests is an Artacc H 400 station (Figure 10). The dumbbells and bars are placed on the turnstile of the aging chamber. A sampling of 3 dumbbells and 3 bars is done at 48 h (2 days), 144 h (6 days) and 240 h (10 days).

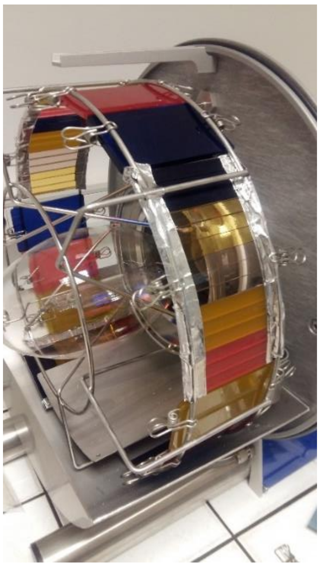


Figure 10: Samples on the turnstile of the accelerated aging chamber Artacc H400

After each aging period, the samples are dried and then used for tensile testing at break and impact resistance.

The detail of the specific test condition and the results of tests performed on the various formulations are added in the confidential version of this deliverable.

V. Processing of semi-finished products

1. Monofilament

Monofilament manufacturing tests are carried out on the SCAMEX extrusion line available at ComposiTIC and the drawing of monofilaments is made possible thanks to the acquisition of a spinning/drawing machine obtained thanks to a call for tender launched by UBS (Figure 11):

Figure 11: extrusion line and drawing machine.

The monofilament is stretched by different heating rollers which rotate at different speeds in order to initiate the orientation of the macromolecular chains in the stretching direction. This step is necessary to improve the mechanical properties of the monofilament.

2. Multifilament

The tests at laboratory scale are carried out at ENSAIT (*Ecole Nationale supérieure des Arts et Industries textiles*) in France (Figure 12). UBS is also equipped with a multifilament die, adaptable to the existing machine (Figure 11) but the first tests showed the need to improve the in-line drawing system to keep up with the speed rates.

Regarding the process parameters, the formulations referenced could be processed (Figure 12). it is a very sensitive process which requires a very specific viscosity at a given temperature.

Figure 12: photographs of the multifilament transformation process

VI. Characterization of filament

1. Mechanical properties

The mechanical properties of both monofilaments and multifilaments are characterized by tensile tests on an Instron 5566A machine, equipped with specific jaws for filaments (Figure 13).

The tests were performed in accordance with the ISO 2062 standard.

Figure 13 : monofilament installed on the traction machine before testing

The results of tests performed on the various formulations is added in the confidential version of this deliverable.

2. Abrasion resistance measurement

The machine used to carry out these tests is an adaptation of the machine described in the ASTM D6611 standard for measuring the abrasion resistance of multifilaments. According to this standard, abrasion is caused by the filament rubbing against itself when subjected to a defined weight and driven by a motor at 1 rpm (Figure 144 left). In this project, a qualitative study was carried out to compare the abrasion resistance of the monofilaments. The main parameters used are as follows:

- 4 different weights: 26 g, 42 g, 71 g, 91 g
- 10 repetitions per weight, same series performed in water immersion.

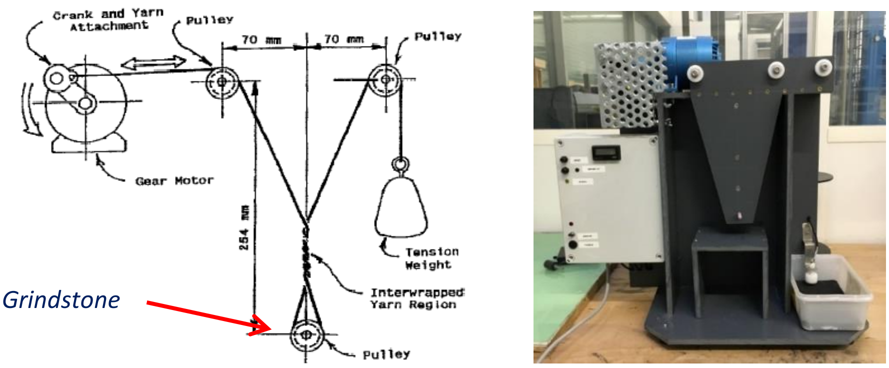


Figure 14: Diagram corresponding to the ASTM standard where abrasion takes place filament against filament (left) and machine used with an abrasive surface instead of a pulley (right)

The results of tests performed on the various formulations is added in the confidential version of this deliverable.

VII. Conclusions

The various stages of development of the semi-finished products in the INdIGO project turn out to be long and time-consuming, but they are nevertheless necessary for the product developed to meet the expectations of the specifications and end-users. The iterative process enabled to increase step by step the properties of the formulation, and to select best polymer candidates and additives. Various formulations were selected for production at lab scale and semi-industrial scale of filaments, and some initial prototypes were developed.

All the tests carried out so far have been promising. However, at each step up, for example at NaturePlast between a laboratory scale extruder and a semi-industrial extruder or between spinning tests at UBS and at the industrial site, new constraints appear, and adjustments are often necessary.

For next step, optimized tests will be made on the formulations to assess their ability to be used to produce fishing gears prototype:

- Monofilament: The production of the monofilament is planned on one selected formulation, and about 50kg of material will be produced. The semi-finished products will then be used to manufacture the fine net, which will be subcontracted task.
- Multifilament: Production of the multifilament is planned on one selected formulation, and about 50kg of material will be produced. The semi-finished products will then be used in the next stage for the production of the net for aquaculture at Filt's.