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# Roboze Bio-based PA

## Overview

Composed of XD10 polyamide (PA) reinforced with natural fibers, Roboze's Bio-based PA is born from a commitment to developing sustainably sourced products with a reduced environmental impact. This techno polymer is composed of up to 60% of components produced from renewable resources (sebacic acid is extracted from crushed castor seeds) and reinforced with natural fibres instead of petroleum-based polyacrylonitrile (PAN) carbon fibres (CFs).
Bio-based PA offers exceptional mechanical strength and stiffness, outstanding thermal p roperties, and a wide chemical resistance. Although not biodegradable, it is recyclable and possesses the same specifications and performance as a petroleum-based PA reinforced with 10% CFs, but with a 60% lower carbon footprint. Thanks to this combination of properties, it enables the most advanced applications while still meeting sustainability goals and helping to contribute to a planet-positive future.

Roboze's Bio-based PA can be printed at a temperature significantly lower than even that of Carbon PA and other PAs, resulting in huge savings in terms of carbon emissions as well as costs in the form of consumed electricity. Bio-based PA also possesses low hygroscopicity, great property retention rate after water uptake, negligible warpage, and excellent dimensional stability. Finally, thanks to its shiny black surface and excellent appearance it is can be used to manufacture aesthetic parts without the need for post-processing.

## Applications

Bio-based PA enables the printing of parts, via fused filament fabrication (FFF), exhibiting a more isotropic behavior when compared to other materials, hence Bio-based PA can be successfully used in many industries. The combination of low water absorption and relatively isotropic mechanical properties enables the manufacturing of parts with complex geometries and excellent mechanical responses which can function well in humid environments.

Star wheel conveyors and grippers used in production lines for containers with fluids are examples of ideal applications for Bio-based PA, where its wide chemical compatibility allows it to be employed in a huge variety of applications. Also, its low hygroscopicity means that when aqueous solutions spill onto the components the water absorption will be minimal, causing only a negligible loss of properties. On top of that, being a relatively isotropic material, parts made with Bio-based PA can be printed in the most convenient orientation to minimise printing time and material use (and therefore cost), without needing to orient the part to maximise the mechanical response.

## Design phase

**The preparation of the samples and the execution of the individual tests followed the guidelines imposed by the associated regulations.[1]**

1 Although data measured in a controlled environment can provide an indication of the chemical/physical and mechanical properties of the material and thus enable comparison between different materials, the results of these tests may not be the same as those observed in the final component.

This phenomenon may be caused by the presence of geometric features or manufacturing conditions that may contribute to modifying the material behaviour. Furthermore, the properties of polymeric materials are a function of both temperature and environmental factors (solar radiation, humidity, etc.), which is why the effect of these variables should also be considered during the design phase, both in the case of short-term and long-term exposure.

In view of the above, it is recommended that a prototype be made in advance during the design phase to empirically verify its properties in the operating conditions required by the specific application.

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## Manufacturing Process

Specimens were manufactured on a Roboze Plus PRO fed with a 1.75 ± 0.05 mm diameter filament. This thermoplastic filament was subsequently extruded through a 0.6 mm diameter nozzle. Before starting the printing process, in order to minimize the amount of water molecules adsorbed and absorbed by the filament due to exposure to the atmospheric environment, Roboze Bio-based PA spools were subjected to a drying cycle at a temperature of 80°C for 12 hours in HT Dryer.

The temperature of the print bed was set to 80°C. Before starting the printing process, 15 minutes of thermal equilibration were allowed.

The printing parameters for the following data are:

- Buildplate Temperature =80°C
- Extrusion Temperature = 225°C
- Printing Speed = 1800 mm/min
- Layer Height = 0.35 mm
- Infill Percentage = 100%

At the end of the printing process the support structures were manually removed.

The additive manufacturing technology produces intrinsically anisotropic components. As the orientation of the component on the printing plate changes, so do both the properties of the final printed part and the productivity of the printing process. Keeping in mind what has been written above, it is possible to identify three different orientations on the building plate that are named as follows:

- Flat (or XY)
- On Edge (or XZ)
- Upright (or ZX)

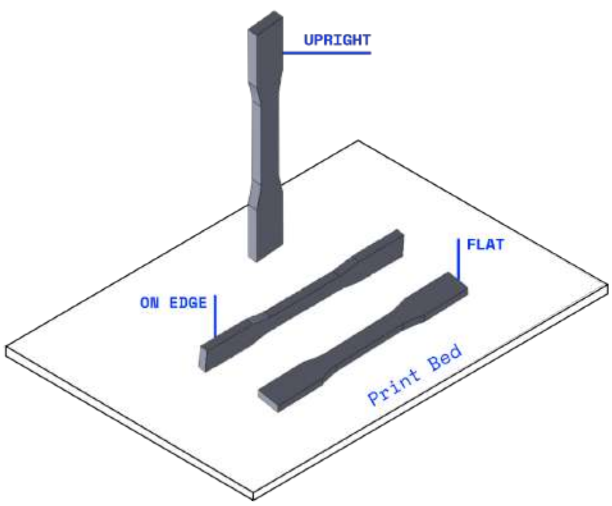


*Figure 1: Example of On Edge, Upright and Flat orientation on the building plate*

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## Summary of the Roboze Bio-based PA properties

### MECHANICAL PROPERTIES

| PROPERTY | OPERATING CONDITIONS | UNITS | ORIENTATION | | | TEST METHOD |
|---|---|---|---|---|---|---|
| | | | XZ | XY ±45° | ZX | |
| Tensile Strength | 25°C | MPa | 66 | 57 | 49 | ASTM D638 |
| Elongation at Break | 25°C | % | 3.6 | 2.6 | 2.5 | ASTM D638 |
| Young's Modulus | 25°C | GPa | 2.6 | 2.7 | 2.2 | ASTM D638 |

### PHYSICAL PROPERTIES

| PROPERTY | OPERATING CONDITIONS | UNITS | VALUE | TEST METHOD |
|---|---|---|---|---|
| Specific gravity | | $g/cm^3$ | 1.12 | ISO 1183 |
| Water Absorption | Weighed sample after: 1) immersion in water for 8 hours at 25 °C; 2) drying in oven for 12 hours at 80 °C | % | 1.2 | Moisture gravimetric content (MGC) method |
| Glass transition temperature ($T_g$) | 20 °C/min heating and cooling rate, in air | °C | 56 | Differential Scanning Calorimetry (DSC) |
| Melting point ($T_m$) | 20 °C/min heating and cooling rate, in air | °C | 183 | Differential Scanning Calorimetry (DSC) |
| CTE (Coefficient of Thermal Expansion), 25 °C – 40 °C | From 25 °C to 800 °C in air flow | $10^{-6}$/°C | 14.4 | Thermo-mechanical Analysis (TMA) ISO 11359 |
| CTE (Coefficient of Thermal Expansion), 90 °C – 140 °C | From 25 °C to 800 °C in air flow | $10^{-6}$/°C | 163 | Thermo-mechanical Analysis (TMA) ISO 11359 |
| HDT (heat deflection temperature) | 1.8 MPa, orientation printed sample XZ | °C | 56.5 | ASTM D648 |
| Colour | | | Shiny black | |

The information may come from the raw material, the semi-finisshed product or an estimate.
Specific individual tests are recommended according to the applicationsconditions required for final implementation.

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## Mechanical Properties

### Tensile Properties

The tensile test is a destructive test useful to characterize the properties of materials when subjected to uniaxial tensile loads. A specimen of standard dimensions, having a "dogbone" geometry, is clamped by means of appropriate clamps to two crossbeams.

The movable crossbeam can move upwards, thus bringing the specimen into a tensile state. Once the displacement speed of the crossbar has been set, the load applied and the deformation undergone by the sample are monitored during the test.

In output the system is able to provide a Cartesian graph where on the ordinates is represented the stress ($\sigma$), i.e. the ratio between the force applied to move the mobile crosshead at constant speed and the minimum section of the "dogbone" test specimen; while the abscissae report the strain ($\varepsilon$), i.e. the percentage ratio between the variation of length of the test specimen with respect to its initial dimensions ($\Delta\ell$) and its nominal length before the start of the test ($\ell_0$).

The stress-strain curve will be a function of the nature of the material. The characteristic parameters that can be derived from this curve are: tensile strength ($\sigma_M$), Young's modulus (E) and elongation at break ($\varepsilon_0$).

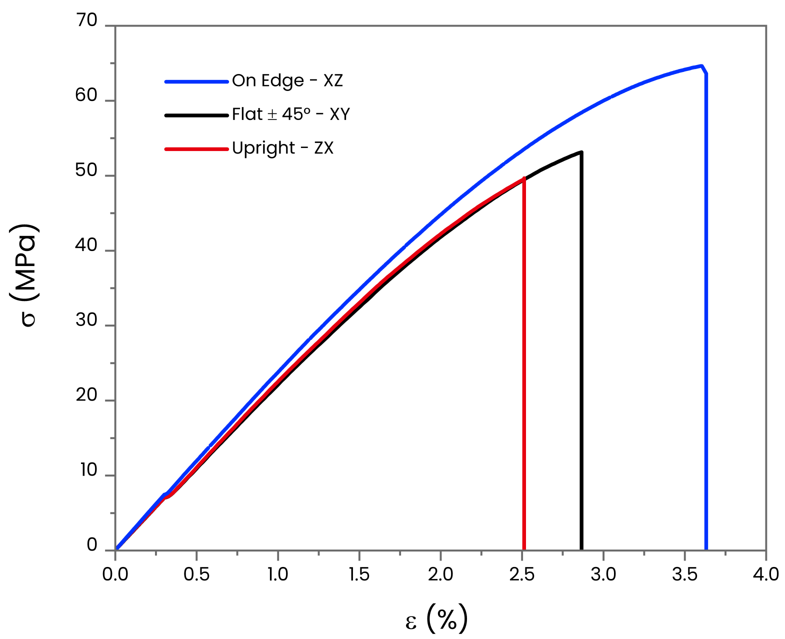


*Figure 2: Comparison between tensile test behaviour of Bio-based PA samples built in different orientations*

The initial section of the curve shows a region of linear elastic deformation. In this region (also called the Hookean region of the material), the material undergoes an instantaneous and reversible strain that is linearly dependent on the applied stress.

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The angular coefficient of the tangent line to the linear elastic region is defined as Young's Modulus, which is the constant of proportionality between the strain undergone by the material and the applied stress. Young's modulus is generally measured from the stresses at 0.05 % and 0.25 % strain. It should be noted that components manufactured by additive manufacturing have anisotropic mechanical properties therefore, particularly with very complex geometries, it can be difficult to maximise the mechanical response. Typically, the best practice is to identify the main load direction and orient the part in relation to this.

The samples were characterised using the ASTM D638 standard. ZX-oriented specimens were milled from a 120x3.2x60 mm plate to evaluate inter-layer adhesion properties with minimal interference from spurious phenomena. A speed of 1 mm/min was used to calculate the tensile modulus, thereafter the speed was increased up to 50 mm/min until the specimen failed. It should be noted that results of tensile testing are a function of test speed, therefore for a proper comparison between different materials it is important to know in advance the speed at which the test was performed.

*Table 1: Tensile properties of Roboze Bio-based PA measured at 25 °C for different specimen orientations*

| PROPERTY | OPERATING CONDITIONS | UNITS | ORIENTATION | | | TEST METHOD |
|---|---|---|---|---|---|---|
| | | | XZ | XY ±45° | ZX | |
| Tensile Strength | 25 °C | MPa | 66 | 57 | 49 | ASTM D638 |
| Elongation at break | 25 °C | % | 3.6 | 2.6 | 2.5 | ASTM D638 |
| Young's Modulus | 25 °C | GPa | 2.6 | 2.7 | 2.2 | ASTM D638 |

## Physical Properties

### Water and moisture absorption

Residual moisture in the filament can lead to several problems during the printing process, it is recommended to dry it for at least 2 hours (and a maximum of 12) at 80 °C before printing. The water molecules adsorbed and absorbed by the material may trigger hydrolysis phenomena during extrusion due to the high temperature of the process. Moreover, even though Roboze's Bio-based PA is less affected than other PAs by moisture absorption, after printing the parts it is good practice to keep them in a dry environment. The reason being that since water behaves as a plasticizer with PAs, technically relevant mechanical parameters (e.g., Young's modulus) of printed parts can be negatively affected by absorbed moisture.

Information about the hygroscopic properties of the material is therefore of particular interest for both an efficient printing process and to predict the final properties of printed parts.

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The moisture gravimetric content (MGC) method consists of weighing a moist sample (exposed to controlled humidity conditions), oven drying it, reweighting, and calculating the mass of water loss as a percentage of the mass of the sample. The MGC is important for applications where the material is exposed to high humidity or is in direct contact with water.

The measured water absorption rate is shown below:

*Table 2: Water absorption of Bio-based PA*

| PROPERTY | OPERATING CONDITIONS | UNITS | VALUE | TEST METHOD |
|---|---|---|---|---|
| WATER ABSORPTION | Weighed sample after:<br>1) immersion in water for 8 hours at 25 °C;<br>2) drying in oven for 12 hours at 80 °C | % | 1.2 | MGC METHOD |

## Melting and glass transition temperatures

Unlike thermosets, when heated thermoplastic polymers undergo a progressive softening process until they reach complete melting. The energy supplied through heat irradiation can weaken and progressively break the van der Waals bonds between the various polymer chains.

This phenomenon involves a reduction in the stiffness of the polymer, which stops behaving as an elastic solid and begins to assume the typical behaviour of a viscoelastic material. The higher the temperature, the greater the viscous component will be compared to the elastic one.

As the temperature rises, the energy supplied to the system increases, causing the carbon chains to start moving. This changes the material from a hard and relatively brittle "glassy" state into a viscous or "rubbery" one, this happens at a temperature known as the glass transition temperature ($T_g$). Further heating allows the progressive dissolution of the crystalline domains, which happens at the melting temperature ($T_m$). The crystalline domains are generated during the cooling of the material, and this happens to a temperature known as crystallization temperature ($T_c$).

The technique that allows to determine the $T_g$ , $T_m$ , and $T_c$ is Differential Scanning Calorimetry (DSC, graph shown in Figure 3). This technique measures the amount of energy absorbed or released by a sample when heated or cooled. The characteristic temperatures of Bio-based PA are given in the following table.

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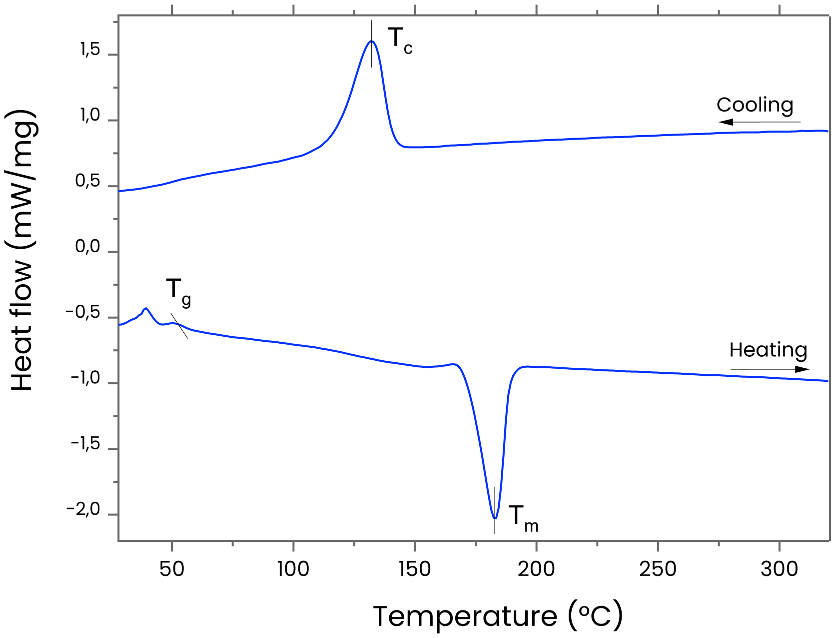


*Figure 3: Differential scanning calorimetry (DSC) graph with a 20 °C/min heating and cooling rate, in air*

*Table 3: Glass transition temperature ($T_g$), melting temperature ($T_m$), and crystallization temperature ($T_c$) of Bio-based PA*

| PROPERTY | UNIT | VALUE | TEST METHOD |
|---|---|---|---|
| MELTING POINT ($T_m$) | °C | 183 | DSC |
| GLASS TRANSITION TEMPERATURE ($T_g$) | °C | 56 | DSC |
| CRYSTALLIZATION TEMPERATURE ($T_c$) | °C | 132 | DSC |

## Coefficient of Thermal Expansion ($\alpha_T$)

When a material in the solid state is subjected to cooling and/or heating cycles it has a tendency to contract/dilate. The phenomenon of expansion of bodies is directly related to the atomic bond force. In fact, by supplying heat to the System, the increase of the vibration amplitude of the atomic bond is favored, thus causing the dilation of the body. The greater the bond force, the lesser the expansion of the material.

The linear coefficient of thermal expansivity ($\alpha_T$) is the length change for an infinitesimally narrow temperature range, at any temperature T, and is defined as follows:

$$\alpha_T = \frac{1}{L_0} \left( \frac{d\,L}{d\,T} \right)_T$$

Where L is the length of the sample, T its temperature, and $L_0$ its initial length. The coefficient of thermal expansion therefore represents the correlation coefficient between the deformation undergone by the material and the temperature variation.

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Knowing $\alpha_T$ for a material is very important when designing parts; a smaller $\alpha_T$ results in more dimensional stability during printing or in high temperature environments.

The coefficient of thermal expansion is dependent on the temperature of the material, especially above $T_g$, therefore a single reported number for $\alpha_T$ will not accurately reflect the expansion behaviour, except below $T_g$ where $\alpha_T$ changes little. Nonetheless, it is customary to select a representative value of αT for comparison purposes.

*Table 4: Coefficient of Thermal Expansion at different temperatures*

| PROPERTY | OPERATING CONDITIONS | UNITS | VALUE | TEST METHOD |
|---|---|---|---|---|
| $\alpha_T$ , 25 °C – 40 °C | FROM 25 °C TO 800 °C IN AIR FLOW | $10^{-6}$/°C | 14.4 | TMA, ISO 11359 |
| $\alpha_T$ , 90 °C – 140 °C | FROM 25 °C TO 800 °C IN AIR FLOW | $10^{-6}$/°C | 163 | TMA, ISO 11359 |

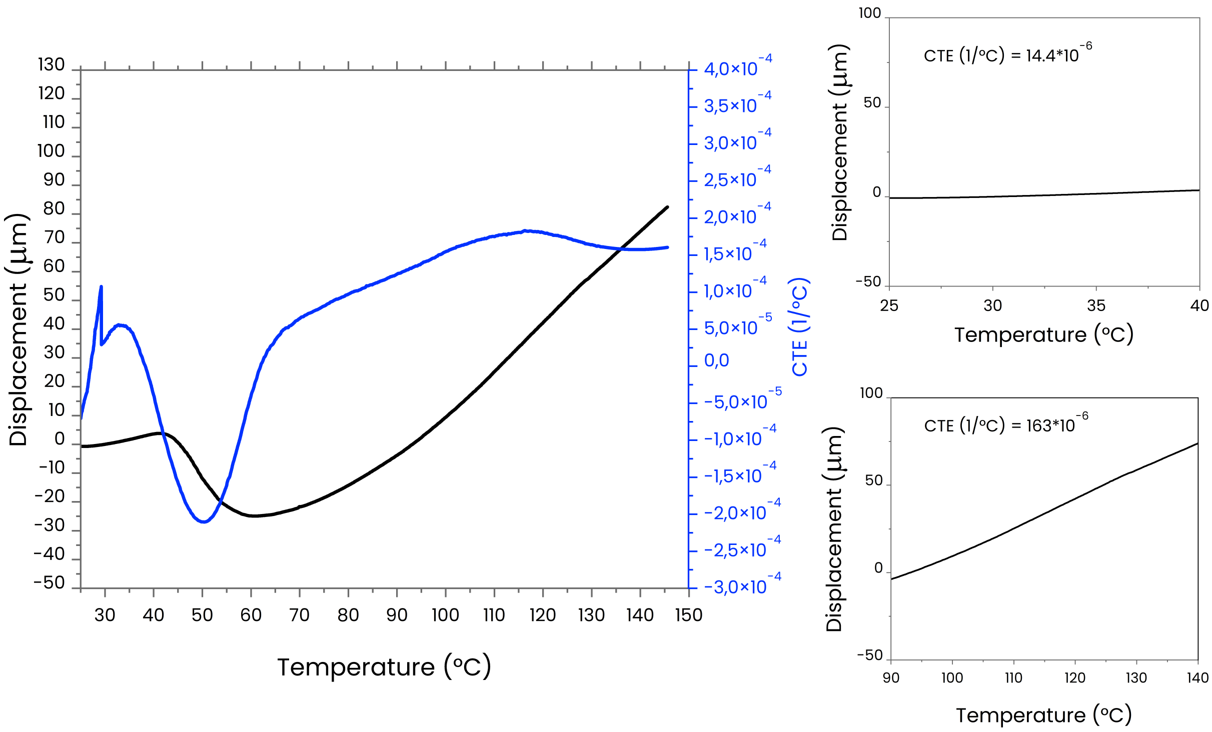


*Figure 4: Displacement and CTE as a function of temperature for Roboze's Bio-based PA*

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## Heat Deflection Temperature (HDT)

The Heat Deflection Temperature (HDT) allows to empirically define the ability of a material to resist a constant stress when exposed to an elevated temperature. The used standard for this analysis is ASTM D648. This standard involves the use of a sample with the shape of a regular quadrangular prism (127 mm x 13 mm x 3.2 mm) placed edgewise on two supports 101.6 mm apart (Method A). The specimen is then loaded with a constant stress of 1.8 MPa. The heating of the sample is achieved by immersing it in a heated fluid bath with a heating rate of 120°C/h.  The temperature at which a deflection of 0.25 mm occurs is defined HDT. The value reported in the table below is an average obtained by testing three identical specimens.

*Table 5: Heat Deflection Temperature for samples printed along XZ orientation*

| PROPERTY | TEST CONDITIONS | ORIENTATION | VALUE | TEST METHOD |
|---|---|---|---|---|
| HDT | 1.8 MPa | XZ | 56.5 °C | ASTM D648 |