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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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1 INTRODUCTION

In this deliverable report the public information about the production of PLA compounds developed at pilot-plant level is reported. In order to do it raw materials, testing standards, and compounding equipment and methodology are reported. The compounds were injection moulded into test specimens and characterized. Finally the technical data sheets of the most promising formulations for the project are compiled.

The case study parts developed within NATURTRUCK project “foot rest” and “bracket” are shown in Figure 1. In Table 1 the initial requirements for the case studies are compiled.

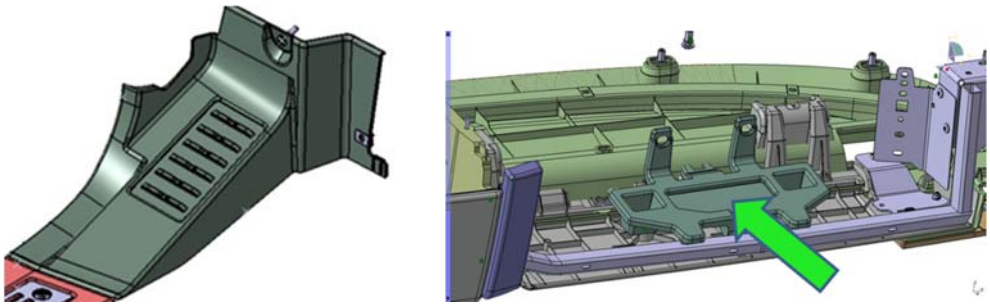

Figure 1. NATURTRUCK case studies. Left: foot rest. Right: bracket.

Table 1. Mechanical and thermal requirements for NATURTRUCK case studies.

Requirement	Foot rest requirements	Bracket requirements	Test method
Tensile Modulus (MPa)	≥2100 MPa	≥1700 MPa	ISO 527-2
Flexural Modulus (MPa)	≥2100 MPa	≥2200 MPa	ISO 178
Charpy Impact 23ºC (kJ/m^2)	≥35 kJ/m^2	≥ 15 kJ/m^2	ISO 179
Charpy Impact -40ºC (kJ/m^2)	≥12 kJ/m^2	≥ 5 kJ/m^2	ISO 179
HDT B (ºC)	105°C	108°C	ISO 75
Flammability	Combustion fastness ≤ 80 mm/min		STD104-0001

According to this table the tensile properties (modulus and strength), impact strength (at 23ºC) and HDT (B) were used to monitor the formulation development within the

project. Whereas the UL94 (horizontal burning test) was used to determine the speed of flame spread is measured in mm/min.

2 MATERIALS

The raw materials used in the formulations reported in this deliverable report are listed below. Some of them were just named in a generic form to preserve the confidentiality of the formulation.

- **PLA INGEO 3260HP**from NATUREWORKS, it is PLA for injection moulding purpose, and high crystallization rate.
- **Hemp fibre pellets** supplied by the project Partner BAVE.
- **Talc** as a nucleating agent.
- **Flame retardant.** Commercial halogen free flame retardant (HFFR) based on micro-encapsulated ammonium polyphosphate.

Other additives that were used in this investigation were common additives like **nucleants**, and **antioxidants** and **chain extenders**. Other materials were also used to improve the impact strength of the biocomposites; **bioplasticizers**, **impact modifiers**, **flexible polyester**, and a **compatibilizer** to improve the compatibility with natural fibres and between biopolymers.

3 METHODOLOGY.

The composites developed within this study were carried out by means of the compounding process by using a pilot plant size twin screw extruder. Then the samples were injected and characterized. The processes are described in the following points.

3.1 Compounding process.

The compounding process was carried out in a co-rotating COPERION ZSK25 twin screw extruder (TSE) with a 25mm of screw diameter and processing length of 40D. This extruder has one side feeder and 3 venting ports (the last one vacuum forced). The compounding line was completed with 2/3 gravimetric feeders, a piston pump (to inject a plasticizer when necessary), and water bath for cooling the strands of molten material and a strand pelletizer (see Figure 2).

Figure 2. Coperion twin screw extruder the compounding process in AIMPLAS pilot plant.

Previous to the compounding process the PLA was dehumidified at 80ºC for 4 hours in, whereas the fibres were dried at 90ºC overnight in and oven to reduce the moisture content of the fibres to <1%wt.

The compounding process was carried out at 10 kg/h and 150 rpm, and the profile temperature from 190 to 175ºC, to 190 - 175ºC in order to reduce the melt temperature and prevent the fibre burning during the process. High vacuum (-0.5 bar) was applied in the final venting port to force the degassing of the molten polymer. The screw configuration was also designed to avoid breaking the fibres in excess, to incorporate the plasticizer in the process, and to avoid the degradation of the fibres during the process.

During the compounding process PLA, fibre pellets, other polymers or additives in masterbatch form were fed through the main hopper in a premix. The mixture is molten in the first section of the extruder. Then a plasticizer is added right after the melting zone of the extruder by a piston pump and through an injection port, and is mixed with the molten material. Then the flame retardant is fed into the extruder through the side feeder, and it is incorporated and dispersed into the molten polymer in the following section of the extruder. Between the venting zones the material is homogenized and then vented in last barrel, where a vacuum pump is installed to remove the volatiles remaining in the molten material. The schemes of the compounding line and extruder configuration are shown in and Figure 3 and Figure 4.

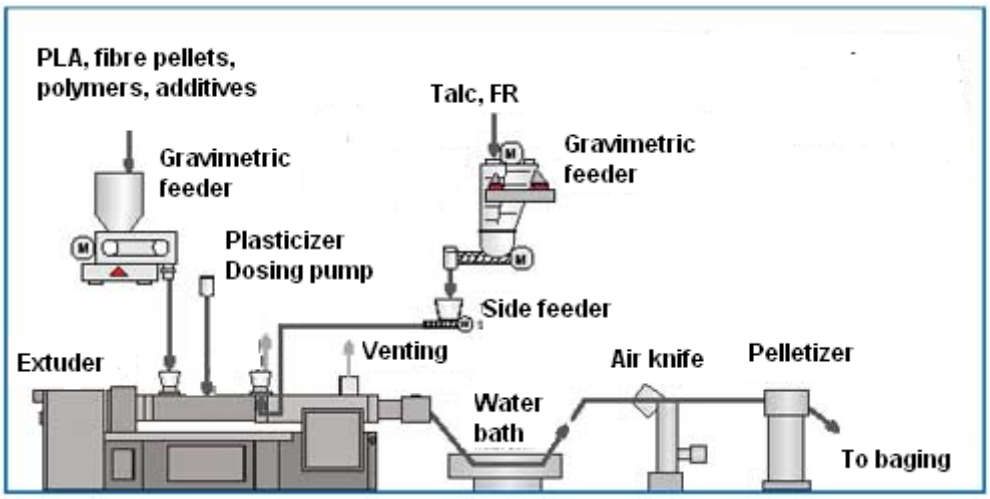

Figure 3. Scheme of the compounding process.

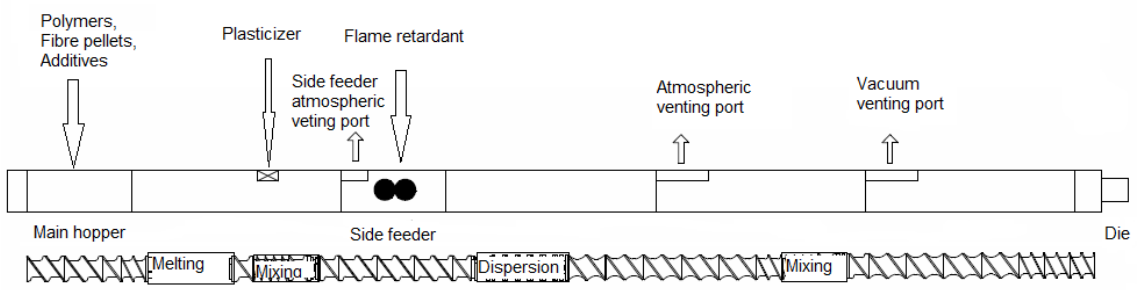

Figure 4. Scheme of the extruder configuration for the compounding process.

Finally the material exits the extruder in the form of molten strands that are cooled in a water bath and cut into pellets (see Figure 5) to be used afterwards in the injection moulding process. The remaining moisture of the pellets was removed by drying them for 4h and 60ºC.

Figure 5. Pellets of PLA with hemp fibres.

3.2 Injection moulding process.

After the compounding process, the biocomposites were moulded into test specimens by injection moulding for characterization purposes (see Figure 6). They were injected in a KRAUSS MAFFEI EX160-750 injection machine with a 160 ton of clamping force and screw diameter of 50mm in order to produce test specimens for flexural and tensile properties, impact properties, heat deflection temperature and UL94 (horizontal burning). Previous to the injection moulding process the pellets were dried at least 4 h at 60º C. All samples were injected using a profile temperature of 150 to 190ºC and mould temperature of 20ºC.

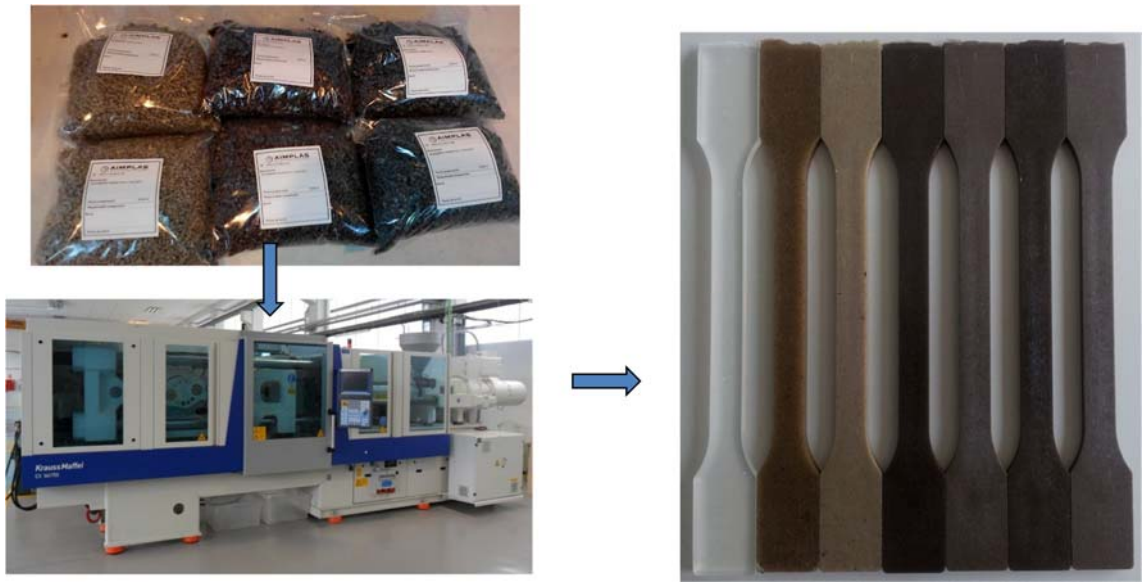

Figure 6. Pellets of PLA composites with different natural fibres, injection moulding machine and injected test specimens. The clear specimens corresponded to raw PLA.

Finally the compounds and injected specimens were characterized. The results are compiled in the technical data sheets of the biocomposites.

3.3 Characterization tests.

The characterization tests carried out over the biocomposites are described in the following points.

- **Melt flow index:** The melt flow index (MFI) was determined according the standard UNE-EN ISO1133-2. The compounds were dried before the test for 4h at 80ºC under vacuum and tested at 190ºC and 5kg.

- **Tensile properties**: tensile strength, tensile strain at break (elongation) and tensile modulus were determined according UNE-EN ISO 527-2 standard.
- **Charpy Unnotched impact strength** at 23º C and -40ºC of the composites was determined according to the standard UNE-EN ISO 179-1.
- **Heat deflection temperature (HDT) method B** (0.45MPa) tests were carried out according to the UNE-EN ISO 75-2
- **Differential scanning calorimetry (DSC):** DSC tests were carried out following the standards UNE-EN-ISO 11357-1, ISO 11357-2 and UNE-EN ISO 11357-3.
- **UL94 Horizontal burning test:** In UL94 test the specimen is supported in a horizontal position and is tilted at 45°. A flame is applied to the end for 30s or until the flame reaches the 25mm (1 inch) mark. If the specimen continues burning after the removal of the flame, the time to burn between the 25 and 100 mm (4 inches) marks are recorded. If the specimen stops burning before the flame spreads to the 100 mm mark, the time of combustion and damaged length between marks is recorded. According to the standard, the material to be rated as HB the specimens must have:
    - A burning rate (or speed of flame spread) < 40 mm/minute for samples with thicknesses between 3 and 13 mm, or < 75 mm/minute for thicknesses < 3 mm over a 75 mm span.
    - Or must stop burning before the flame reaches the 100 mm mark.

  In both cases the materials HB rated are considered "self-extinguishing".

4 RESULTS AND TECHNICAL DATA SHEETS.

4.1 General findings.

In general, PLA/natural fibre composites showed very good tensile properties (stiff and resistant materials) but also had low impact properties (brittle materials). Hemp fibre pellets were selected due to its better handling and feeding accuracy to the extruder in comparison with cut fibres. However fibre pellets must be fed through the main hopper to improve the fibre dispersion in the composite.

The addition of a nucleating agent, for example talc, was necessary to improve the crystallization of the PLA and therefore the mechanical and thermal performance of the composites.

The use of antioxidants was recommended to improve the thermal stability or the PLA/natural fibre composites, and to widen the processing window for the injection moulding process.

Commercial halogen free flame retardant (HFFR) reduced the flammability of PLA/natural biocomposites effectively at addition levels above 12wt% in the composites.

Based on these findings, a formulation of PLA+15wt% hemp fibre +5wt% of talc and 14wt% of FR was selected for further optimization. However, this formulation showed HDT values (as injected) about 57ºC for crystallinity content (in PLA basis) of 23%. This value was increased to 136ºC for the crystallized composite after annealing treatment using microwaves as energy source for heating. In this case the crystallinity increased to 74%. The physical and mechanical properties, HDT(B) and flammability of this composite are shown in Table 2

Table 2. Technical data sheet of selected PLA/hemp composite with talc and FR..

PLA+HEMP(15%)+TALC(5%)+FR(14%). Biocontent = 81wt%		
Property	**As injected**	**Standard**
Tensile modulus (MPa)	6610 ± 87	UNE-EN ISO 527-2
Tensile strength (MPa)	64.4 ± 1.2	UNE-EN ISO 527-2
Elongation (%)	1.2 ± 0.1	UNE-EN ISO 527-2
Charpy Unnotched impact strength (KJ/m^2)	13 ± 1	UNE-EN ISO 179-1
HDT (B) (0.45MPa) (ºC)	57.3 ± 0.2	UNE-EN ISO 75-2
Melt flow index (190ºC, 5kg)	8.3± 0.3	UNE-EN ISO1133-2
Speed of flame spread (mm/min)	22± 5	UL94, HB

4.2 Formulations with plasticizers and impact modifiers

In order to improve the impact strength and flowability of the composites different modifications were carried out over the selected formulation. In this case the formulation was modified with a bioplasticizer and an impact modifier. The objective was double, in one hand to improve the impact strength of the composite, an in the other hand to promote the chain mobility of the PLA to increase the crystallization speed of the PLA.

The addition of plasticizers resulted in an increase of MFI, a reduction of tensile properties, and an improvement of the impact strength of the composites. And the incorporation of an impact modifier resulted and additional increase of impact strength in the plasticized formulation.

This formulation was also modified with the incorporation of a chain extender additive to avoid the hydrolysis of PLA during processing (due to remaining moisture in the fibres and FR). This additive has a positive effect in the impact properties of the composites and a negative effect in the MFI (higher viscosity).

It must be highlighted that the reported mechanical properties were measured over non-annealed tensile test specimens after injection moulding at room temperature (20 – 25ºC). To improve the thermal properties of the biocomposites the injected samples were annealed in an infrared (IR) oven. After annealing the crystallinity was increased to about 60% and the HDT (B) up to 119ºC. As expected, after annealing the tensile modulus of the composite was improved, whereas the tensile and impact strength were slightly reduced, but still met the impact strength requirement.

The technical data sheet of selected composite is showed in Table 3. In this formulation the 79wt% of the raw materials employed in this formulation are from renewable resources.

Table 3. Technical data sheet of selected PLA/hemp/FR composite with plasticizer and impact modifier obtained in the COPERION ZSK25 extruder.

PLA + HEMP(15%) + FR(14%) plasticized and impact modified. Biocontent = 79%			
Property	**As injected**	**Annealed**	**Standard**
Density (g/cm^3)	1.303 ± 0.001	1.302 ± 0.001	UNE-EN ISO 1183
Flexural modulus (MPa)	3240 ± 65	2780 ± 617	UNE-EN ISO 178
Tensile modulus (MPa)	2680 ± 77	2480 ± 100	UNE-EN ISO 527-2
Tensile strength (MPa)	38.9 ± 0.3	39.6 ± 0.1	UNE-EN ISO 527-2
Elongation (%)	3.2 ± 0.1	5.1 ± 0.1	UNE-EN ISO 527-2
Charpy Unnotched impact strength a 23ºC (KJ/m^2)	20 ± 2	23 ± 2	UNE-EN ISO 179-1
Charpy Unnotched impact strength at -40ºC (KJ/m^2)	15 ± 1	14 ± 2	UNE-EN ISO 179-1
HDT (B) (0.45MPa) (ºC)	40.1 ± 0.1	119.6 ± 2.8	UNE-EN ISO 75-2
Flammability. Speed of flame spread (mm/min)	37.7 ± 1.6 (HB)	24.6 ± 8.4 (HB)	UL94, HB

Taking into account these results all mechanical, HDT and flammability requirements for both case studies were achieved with the only exception impact strength a 23ºC for the case study “foot rest”, which was 35kJ/m^2.

Despite the MFI of the composite was 10g/10min, below the required value of 15g/10 min (190ºC and 5kg), the flowability of the composite was good compared with raw ABS, ABS/PC, PLA and commercial PLA with wood fibres (KARELINE). All of them had theoretically higher MFI than NATURTRUCK composites. However, after flow test in a spiral injection mould, NATURTRUCK composite showed a flow length similar to raw PLA and longer than commercial ABS and ABS/PC currently used in automotive parts (see Figure 7).

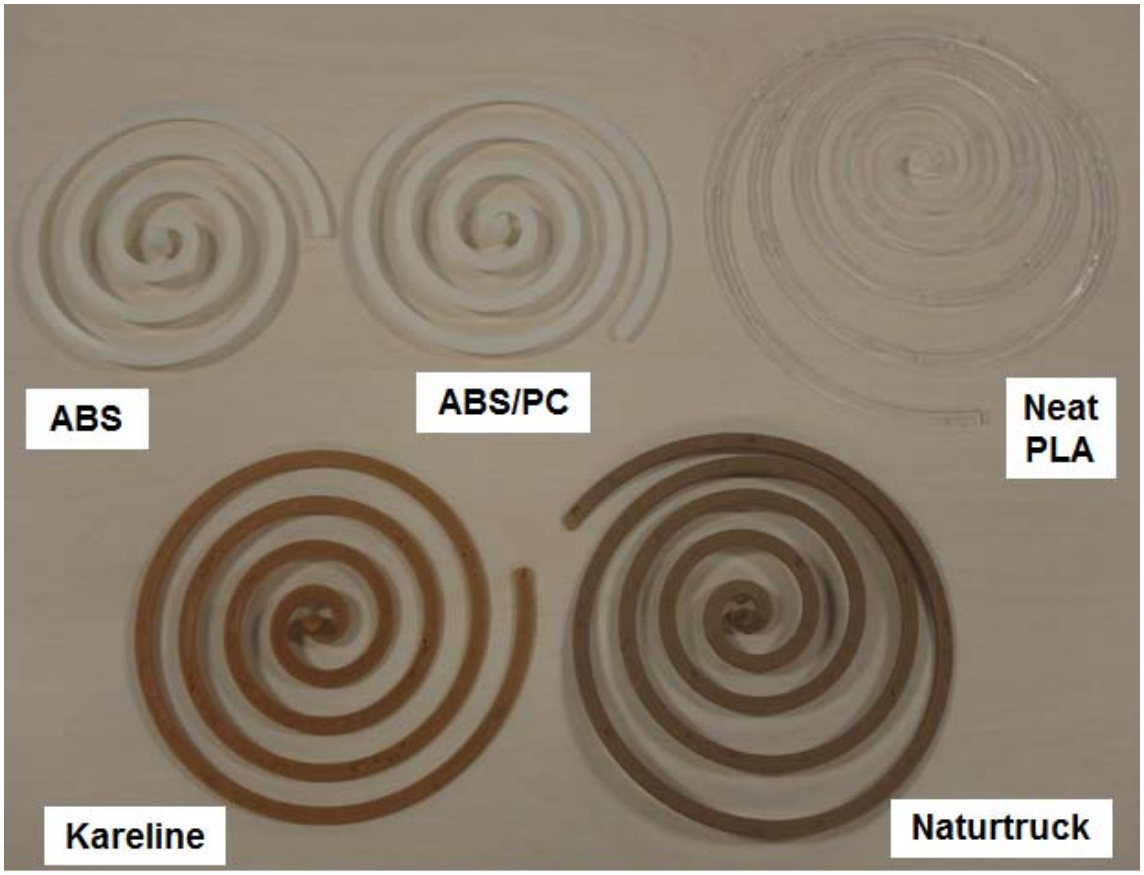

Figure 7. Results of flow test in spiral mould.

4.3 Formulations with blends

Starting with the formulation of PLA+HEMP(15%)+FR(14%), a different approach was chosen to improve the toughness of PLA instead of using plasticizers. This approach consisted in blending PLA with non-biobased flexible thermoplastic polyester.

Different blends were prepared. The introduction of the flexible polyester resulted in a progressively reduction of the tensile properties of the composites, however these properties were superior to PLA composites with plasticizers.

Concerning the impact properties, the impact strength was only minimal improved with the addition of the flexible polyester, and the HDT(B) of non-annealed composites where kept in similar values to the raw PLA (55 – 57ºC).

Finally a blend ratio of PLA/flexible polyester was chosen in a proportion resulting in a 64% of raw materials from renewable resources. The technical data sheet of selected biocomposite is showed in Table 4, in which the properties of the annealed composite were also showed.

Table 4. Technical data sheet of selected PLA/natural fibre composite.

PLA/polyester blend +HEMP(15%)+ FR(14%) **Biocontent = 65%**			
Property	**As injected**	**Annealed**	**Standard**
Tensile modulus (MPa)	4120 ± 167	4530 ± 270	UNE-EN ISO 527-2
Tensile strength (MPa)	47.9 ± 0.3	47.9 ± 0.1	UNE-EN ISO 527-2
Elongation (%)	2.2 ± 0.1	2.2 ± 0.1	UNE-EN ISO 527-2
Charpy Unnotched impact strength (KJ/m^2)	15 ± 1	13 ± 2	UNE-EN ISO 179-1
HDT (B) (0.45MPa) (ºC)	56.7 ± 0.3	101.9 ± 2.2	UNE-EN ISO 75-2
Melt flow index (190ºC, 5kg)	6.4± 0.2	-	UNE-EN ISO1133-2
Speed of flame spread (mm/min)	0	23	UL94, HB

Summarizing, the blend formulation of PLA/polyester +HEMP(15%)+FR(14%) met the mechanical requirements before the annealing treatment for the “bracket” case study, but the compound had high viscosity. The tensile properties and the HDT (B) were improved after the annealing treatment resulting in a HDT (B) > 100ºC, however the impact strength was reduced below the requirement of 15kJ/m^2.

Finally the PLA/polyester blend was modified by partially substitution of the flexible polyester by a compatibilizer. The aim was to compatibilize both polymer phases between them and with the fibres and flame retardant. Moreover the FR content was reduced to 13% as the composite had margin for FR reduction.

The result was an improvement in the impact strength of the biocomposite up to 19kJ/m^2. Therefore the threshold of 15kJ/m^2 of impact strength at room temperature for the case study “bracket” was achieved. This sample also fulfilled the impact requirement at low temperature and the UL94, where the speed of flame spread was 0mm/min. The results were compiled in Table 5. In this case the renewable content was about 64.wt%.

Table 5. Technical data sheet of selected PLA/polyester/compatibilizer composite with hemp fibres and FR.

PLA/flexible polyester/compatibilizer + HEMP(15%) + FR(13%) Biocontent = 64wt%		
Property	**As injected**	**Standard**
Density (g/cm^3)	1.312 ± 0.001	UNE-EN ISO 1183
Flexural modulus (MPa)	4000 ± 200	UNE-EN ISO 178
Tensile modulus (MPa)	3850 ± 185	UNE-EN ISO 527-2
Tensile strength (MPa)	48.6 ± 0.7	UNE-EN ISO 527-2
Elongation (%)	2.6 ± 0.2	UNE-EN ISO 527-2
Charpy Unnotched impact strength a 23ºC (KJ/m^2)	20 ± 2	UNE-EN ISO 179-1
Charpy Unnotched impact strength at -40ºC (KJ/m^2)	19 ± 2	UNE-EN ISO 179-1
HDT (B) (0.45MPa) (ºC)	55.7 ± 0.5	UNE-EN ISO 75-2
Flammability. Speed of flame spread (mm/min)	0 (HB)	UL94, HB

5 CONCLUSIONS

The mechanical, thermal and flammability requirements for the case studies were achieved with the exception of impact strength at room temperature for the case study “foot rest”. The requirements at low temperature were also achieved.

The content of renewable materials goes from 64 to 79wt% for the different formulations.

The formulation of PLA with plasticizer and impact modifier was selected for injection moulding of case study parts due to the good flowability showed in the spiral moulding test.

The best tensile properties were achieved with blends of PLA/flexible polyester/compatibilizer with natural fibres and flame retardants. However this formulation had reduced MFI and therefore was more difficult to inject in comparison with the plasticized formulation.

6 FUTURE WORK

The main efforts in future experiments will be focused in the improvement of the impact strength of the biocomposites to achieve the impact requirements of both case studies.