



## **Sustainpack**

Project no: **500311-2**

Instrument: **IP**

### **D5.49+D5.50 - Report on the mechanical characterization of composites (UDG) (month 36/42).**

Nature of deliverable: **R**

Dissemination level: **PU**

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Start date of project: **2004-06-01**

Duration: **4 years**

Organisation name of lead contractor for this deliverable: **UNIVERSITAT DE GIRONA  
(UdG)**

## **Tasks that have been carried out**

First of all we would like to justify the delay in the delivery of the corresponding reports D5.49 and D5.50. The reason is that we did not have stock of polymer matrices from Novamont. We ordered them during the SP5 meeting, hosted at Verona (April 2007) and until November 2007 we did not received them. Moreover, during the period month 30-36 we received just a set of fibres from STFI partner. We prepared the corresponding composites but the mechanical properties results were impossible to be interpreted (irreproducible). We discussed the problem with the member of STFI (Fredrik Berthold) and we asked them a new stock of fibres to repeat the experiments, but it is not possible. After month 36 we have received new fibres and the corresponding composites are used for the preparation of D5.49 and D5.50.

All of the formulation of composites based on PLLA, starch and polyester (Materbi, Novamont) have been obtained following the methodology that was describe in deliverable D5.10, prepared by UdG group. The used reinforcing percentage was 30 wt% in all of the cases, regarding the whole weight of the composite. The materials were mixed in a Brabender internal mixer (80 rpm and 185° C for PLLA/140° C for polyester Materbi/165° C starch Materbi). The composites were pelletised and processed by injection-moulding to obtain specimens for mechanical testing (tensile, flexural, impact).

The fibres that were used as reinforcement for the preparation of the corresponding composites were received by the following partners: STFI (Sweden) and University of Aveiro (Portugal). The label and the nature of the submitted fibres are showed in table 1.

**Table 1.** Fibres submitted by the corresponding partner for preparing reinforced composites.

Reference	Fibrous reinforcement
<b>University of Aveiro</b>	
Hybrid 1	Cellulose/TiO <sub>2</sub>
Hybrid 2	Cellulose/OTMS/TiO <sub>2</sub>
Blank	Bleached kraft pulp from Eucaluptus Glubulus
<b>STFI</b>	
BTCA	Reference
BTCA 225	heat treated BTCA fibres
BTCA 10%	Pretreated with 10% alkali, heat treated
BTCA 18%	Pretreated with 80% alkali, heat treated

Depending on the specifications of the fibres and the suggestions of the corresponding partners, the polymer matrices were used as follows:

- the fibres submitted by STFI were used as reinforcement of PLLA, polyester and starch (Materbi, Novamont).
- In the case of the fibres developed by the group of the University of Aveiro, they were only used with polyester Materbi due to the lower processing temperature needed for mixing and consolidation.

The composites that were prepared by means of mixing the fibres and the corresponding polymer matrices are summarised in table 2.

**Table 2.** Composites based on PLLA and different fibres provided by STFI

<b>Label</b>	<b>Polymer matrix</b>	<b>Fibrous reinforcement</b>
<b>UNIVERSITY OF AVEIRO</b>		
P <sub>hybrid 1</sub>	Polyester Materbi	Hybrid 1
P <sub>hybrid 2</sub>	Polyester Materbi	Hybrid 2
P <sub>blank</sub>	Polyester Materbi	Blank
<b>STFI</b>		
S <sub>BTCA</sub>	Starch Materbi	BTCA
S <sub>BTCA225</sub>	Starch Materbi	BTCA 225
S <sub>BTCA10</sub>	Starch Materbi	BTCA 10%
S <sub>BTCA18</sub>	Starch Materbi	BTCA 18%
P <sub>BTCA</sub>	Polyester Materbi	BTCA
P <sub>BTCA225</sub>	Polyester Materbi	BTCA 225
P <sub>BTCA10</sub>	Polyester Materbi	BTCA 10%
P <sub>BTCA18</sub>	Polyester Materbi	BTCA 18%
PL <sub>BTCA</sub>	PLLA	BTCA
PL <sub>BTCA225</sub>	PLLA	BTCA 225
PL <sub>BTCA10</sub>	PLLA	BTCA 10%
PL <sub>BTCA18</sub>	PLLA	BTCA 18%

## **RESULTS**

The results will be divided in to main groups depending on the nature of the fibres:

Group 1: Fibres submitted by University of Aveiro;

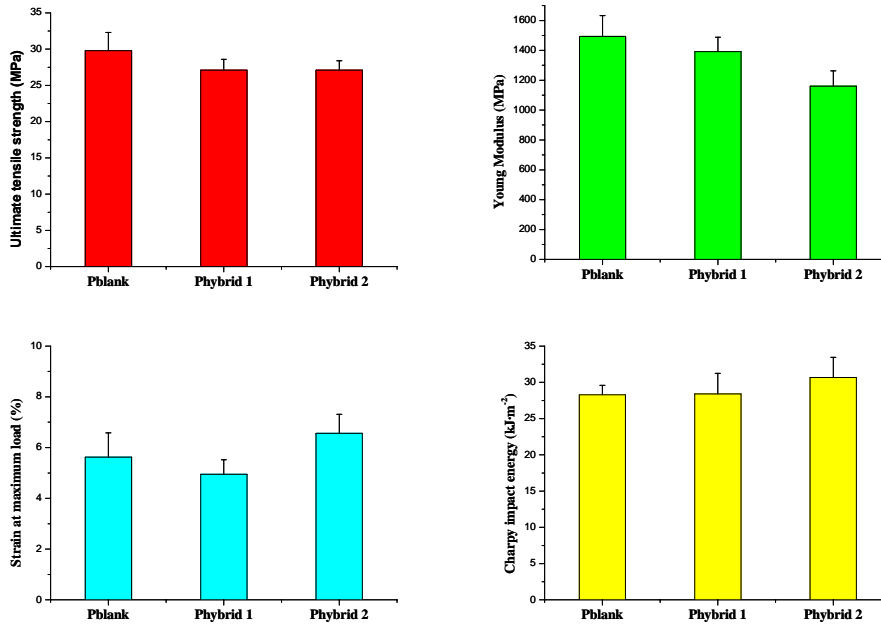
Group 2: Fibres submitted by STFI

At the end of the report an annex will be attached with all of the tables with the values of each mechanical property along with its standard deviation.

### **Group 1**

By indication of University of Aveiro, only polyester Materbi was used as polymer matrix. Different mechanical experiments were carried out in order to characterise the

behaviour of the modification of the fibres. Figure 1 shows the ultimate tensile strength, young modulus, strain at break and impact strength (it means tensile and impact assays) of the three formulations based on polyester Materbi with 30 wt% of fibres.

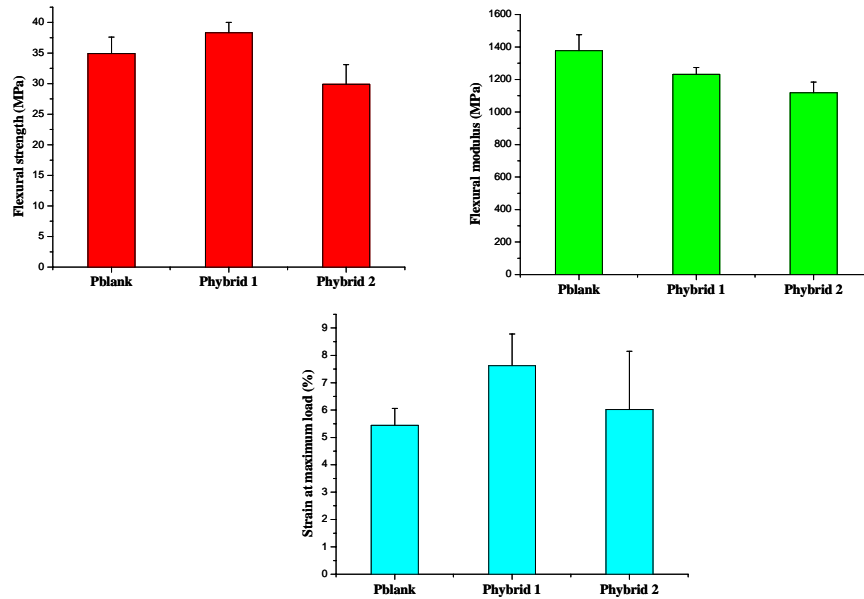


**Figure 1.** Mechanical properties under tensile and impact tests of composites reinforced with hybrid fibres compared to those reinforced with non modified fibres ( $P_{\text{blank}}$ ).

The ultimate tensile strength undergoes a short decrease due to the modification of the fibres with both coatings although this decrease is not significant due if the error bars are considered the average of each material is overlapped. A similar value of the UTS can be related with the acquisition of a similar interface between the polymer and the reinforcement. Hence, the coating of the fibres did not produce a significant loss of tensile resistance.

If Young Modulus is observed a decrease is observed due to the coating of the fibres. Along with this result an increase in the impact resistance is obtained. Due to both results is possible to affirm that the systems reinforced with the hybrid fibres have lower stiffness and they have a higher capacity to absorb impacts. In the case of the formulation reinforced with hybrid 2 reinforcement (cellulose/OTMS/TiO<sub>2</sub>) this effect is acuter due to the value of strain maximum load is even higher than that of composites reinforced with non-modified fibres (blank).

The flexural assay is summarised in figure 2 observing the trend of the flexural strength, flexural modulus and strain at maximum load.

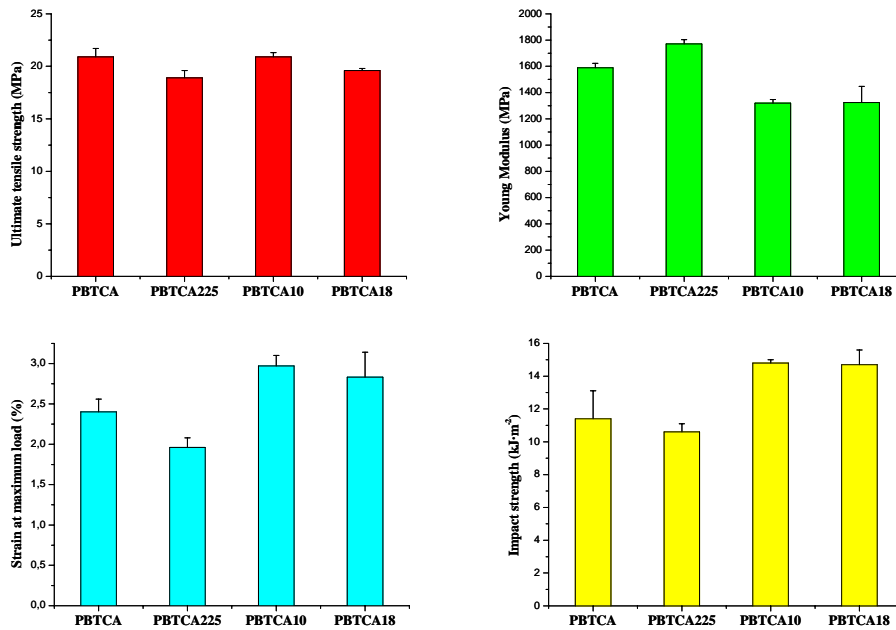


**Figure 2.** Mechanical properties under flexural test of composites reinforced with hybrid fibres compared to those reinforced with non modified fibres (P<sub>blank</sub>).

There are some differences and similarities comparing both tensile and flexural tests. In the case of the moduli, in both cases the same results is obtained due to the coating of the fibres by the inorganic component. In both cases a decrease in the stiffness is obtained along with the increase in the deformation (strain at maximum load). But in the case of the flexural strength the formulation reinforced with hybrid 1 (cellulose/TiO<sub>2</sub>) has a higher value of this property. This value can be assumed as correct due to the very low standard deviation between the individual values. The formulation reinforced with hybrid 2 again has a value of flexural strength lower than that of blank, corresponding a slight loss of compatibility with the polymer matrix.

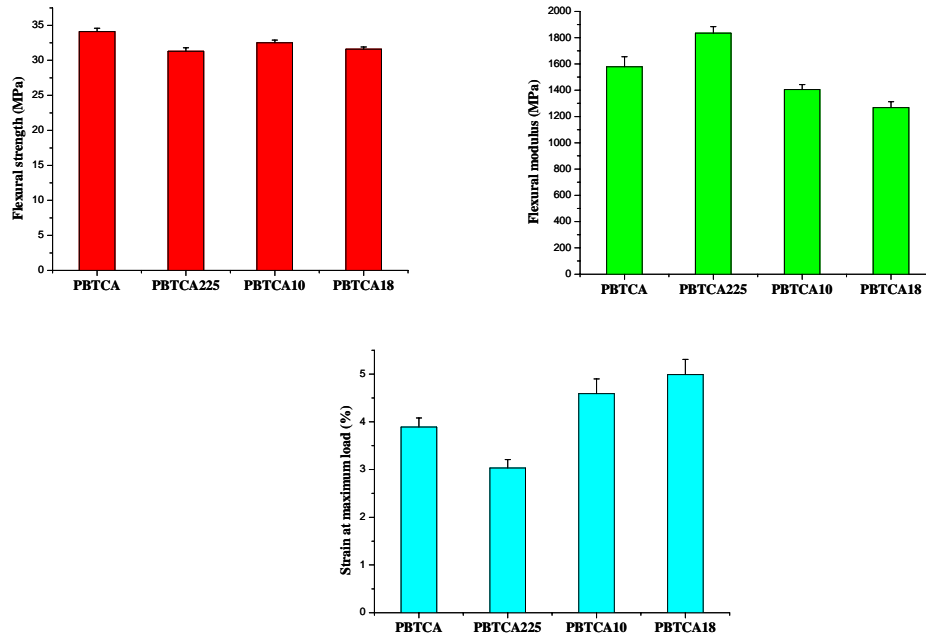
## Group 2

In the case of the fibres modified by STFI group the results under tensile and flexural stresses are analogous, so the comments will be taken into account both together. The results under tensile and flexural stresses of the composites based on polyester Materbi are showed in figure 3 (tensile/impact) and figure 4 (flexural).



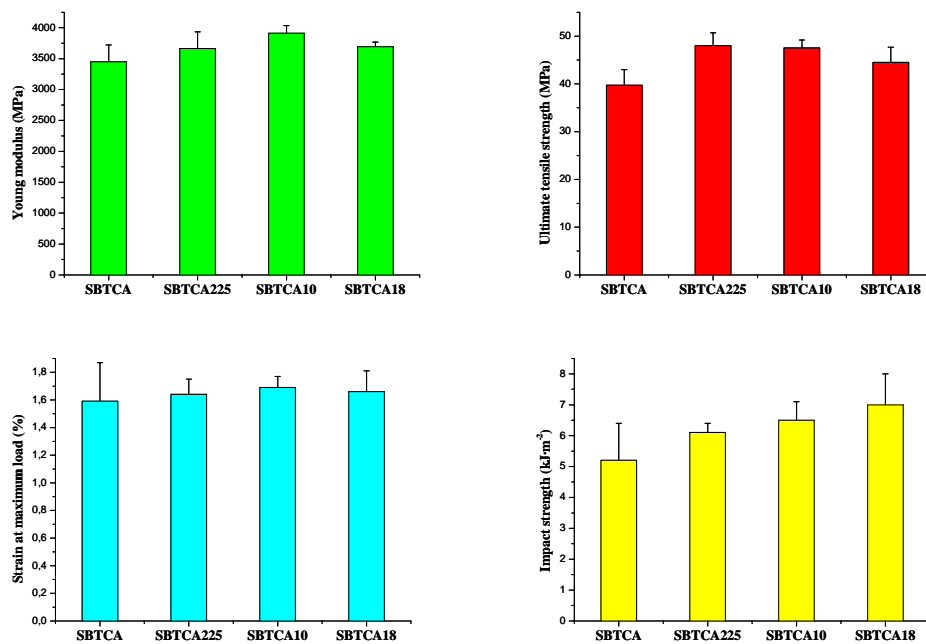
**Figure 3.** Mechanical properties under tensile and impact tests of polyester Materbi-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres ( $P_{BTCA}$ ).

The heat and heat/alkali treatments produced a slight decrease in the ultimate tensile and flexural strengths. It is possible that the surface modification carried out on the fibre produced a decrease in the polymer/fibre interaction. At this moment is not possible to determine if the decrease is related to a change in the chemical structure of the surface of the fibre or a change on its physical structure (roughness and porosity). In the case of the moduli both of them were improved for the formulation heat treated by the alkali treatment harmed the stiffness of the system. According with these results an improvement in the deformability and capacity to absorb impacts is induced to these formulations observed through the results of strain at maximum load and impact strength. This trend in the capacity to absorb impacts is similar for all of the composites (polyester Materbi, starch Materbi and PLLA).



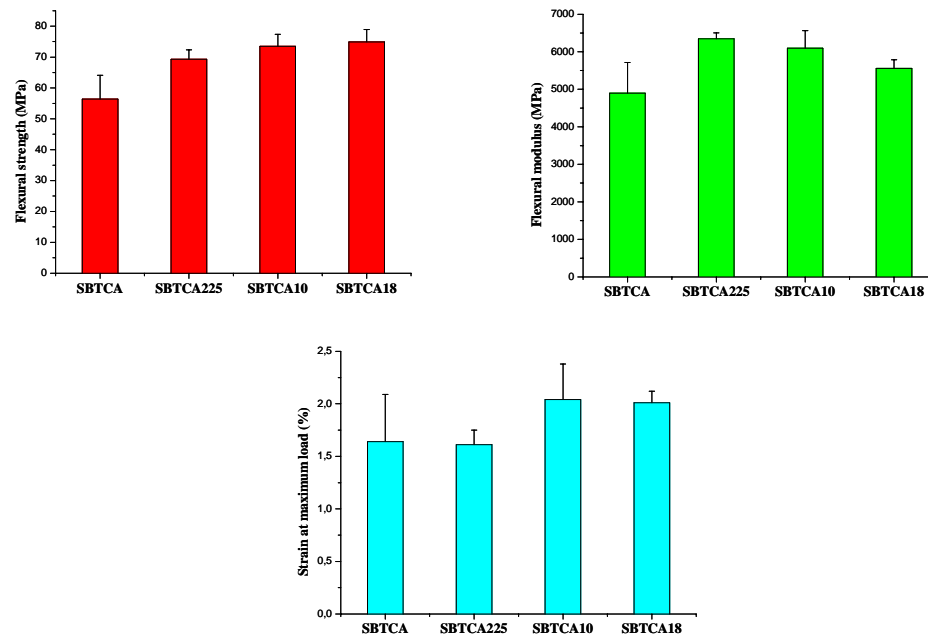
**Figure 4.** Mechanical properties under flexural of polyester Materbi-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres (P<sub>BTCA</sub>).

For the case of the materials prepared with starch Materbi (Novamont) all of them showed a better behaviour than the formulation reinforced with BTCA (S<sub>BTCA</sub>). Tensile and flexural strengths, moduli, strain at maximum load and impact strength were improved indicating that the compatibilisation matrix-fibres is improved by the applied treatments (figures 5 and 6).



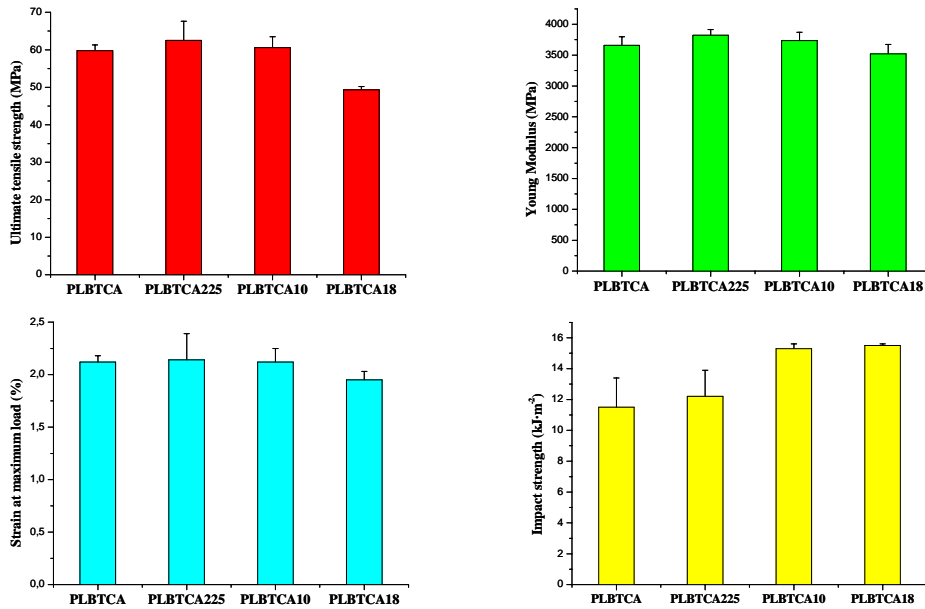
**Figure 5.** Mechanical properties under tensile and impact tests of starch Materbi-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres (S<sub>BTCA</sub>).

Taking in to account the nature of the treatments the heat as well as alkali treatments can remove the impurities on the fibre (rests of lignin (due to it degrades below 225° C), pectins, hemicellulose). This removal of impurities enriches the cellulosic phase of the fibres. As cellulose and starch have –OH groups in their structures an hypothetical improvement in the (OH)starch-(OH)cellulose interaction can be produced.



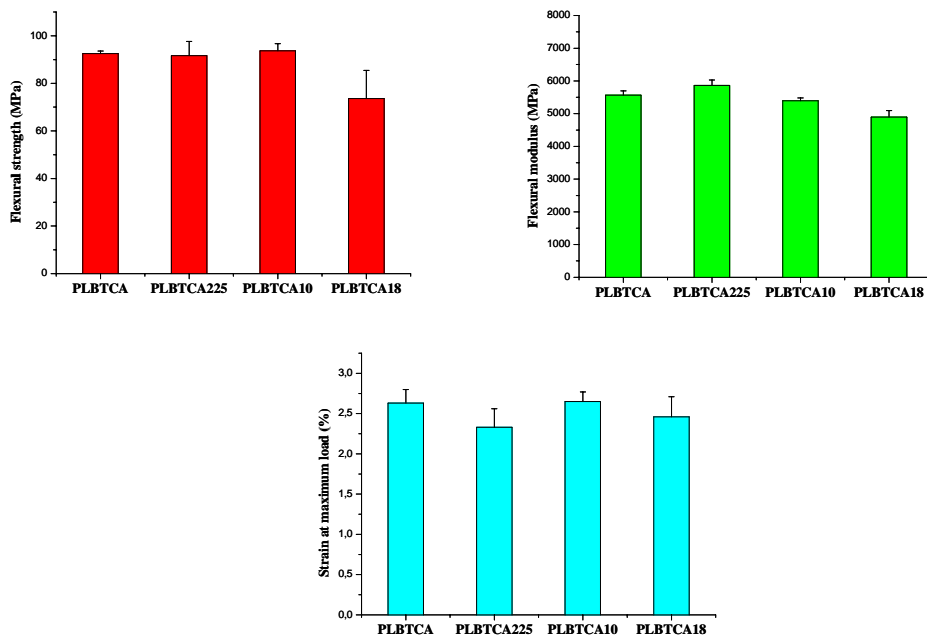
**Figure 6.** Mechanical properties under flexural of starch Materbi-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres ( $S_{BTCA}$ ).

PLLA was the polymer matrix that had the lower influence in the mechanical properties. No trend has been observed due to the modification (except for impact strength as mentioned above). The results under tensile/impact and flexural stresses are summarised in figure 7 and figure 8.



**Figure 7.** Mechanical properties under tensile and impact tests of PLLA-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres (PL<sub>BTCA</sub>).

The heat treatment as well as the milder alkali treatment (10%) did not produce significant changes in the mechanical properties. But the formulation reinforced with BTCA18% gave rise to a decrease in ultimate strengths and moduli. Again the impact resistance was improved.



**Figure 8.** Mechanical properties under flexural of PLLA-based composites reinforced with STFI fibres compared to those reinforced with BTCA fibres (PL<sub>BTCA</sub>).

In general terms, the proposed surface modifications of the fibres of this group 2 have a good influence when are reinforced starch Materbi. In the case of aliphatic polyesters, such as polyester Materbi or PLLA, this influence is slight negative or null.

## ANNEX 1

### Tensile test

	$\sigma_t$ (MPa)	sd	$E_t$ (MPa)	sd	$\varepsilon_{max}$ (%)	sd
PESTER + BLANK	29,8	2,5	1493	140	5,62	0,96
PESTER + HÍBRID 1	27,1	1,5	1392	96	4,95	0,57
PESTER + HÍBRID 2	27,1	1,3	1160	103	6,56	0,75

### Flexural test

	$\sigma_f$ (MPa)	sd	$E_f$ (MPa)	sd	$\varepsilon_{max}$ (mm)	sd
PESTER + BLANK	34,9	2,7	1377	99	5,44	0,62
PESTER + HÍBRID 1	38,3	1,7	1231	42	7,62	1,16
PESTER + HÍBRID 2	29,9	3,2	1118	66	6,02	2,13

### Impact test

	Charpy (KJ/m <sup>2</sup> )	
	sd	
PESTER + BLANK	28,28075	1,314198203
PESTER + HÍBRID 1	28,4034	2,834804896
PESTER + HÍBRID 2	30,6663333	2,790159756

**Annex 1.1.** Numerical results of the mechanical properties of the composites reinforced with the fibres submitted by University of Aveiro.

**Tensile test**

	$\sigma_t$ (MPa)	sd	$E_t$ (MPa)	sd	$\epsilon_{max}$ (%)	sd
P <sub>BTCA</sub>	20,9	0,8	1589	34	2,40	0,16
P <sub>BTCA225</sub>	18,9	0,7	1770	33	1,96	0,12
P <sub>BTCA10</sub>	20,9	0,4	1319	28	2,97	0,13
P <sub>BTCA18</sub>	19,6	0,2	1324	123	2,83	0,31
S <sub>BTCA</sub>	39,7	3,3	3449	273	1,59	0,28
S <sub>BTCA225</sub>	48,0	2,7	3664	269	1,64	0,11
S <sub>BTCA10</sub>	47,5	1,7	3910	125	1,69	0,08
S <sub>BTCA18</sub>	44,5	3,2	3691	77	1,66	0,15
PL <sub>BTCA</sub>	59,8	1,5	3657	141	2,12	0,06
PL <sub>BTCA225</sub>	62,5	5,1	3820	94	2,14	0,25
PL <sub>BTCA10</sub>	60,6	2,9	3735	134	2,12	0,13
PL <sub>BTCA18</sub>	49,3	0,9	3519	153	1,95	0,08

**Flexural test**

	$\sigma_f$ (MPa)	sd	$E_f$ (MPa)	sd	$\epsilon_{max}$ (mm)	sd
P <sub>BTCA</sub>	34,1	0,5	1578	76	3,89	0,19
P <sub>BTCA225</sub>	31,3	0,5	1833	51	3,03	0,18
P <sub>BTCA10</sub>	32,5	0,4	1405	38	4,59	0,31
P <sub>BTCA18</sub>	31,6	0,3	1267	45	4,99	0,32
S <sub>BTCA</sub>	56,4	7,7	4898	816	1,64	0,45
S <sub>BTCA225</sub>	69,3	3,0	6345	158	1,61	0,14
S <sub>BTCA10</sub>	73,5	3,9	6092	472	2,04	0,34
S <sub>BTCA18</sub>	74,9	4,0	5557	231	2,01	0,11
PL <sub>BTCA</sub>	92,5	1,1	5564	132	2,63	0,17
PL <sub>BTCA225</sub>	91,6	6,0	5864	163	2,33	0,23
PL <sub>BTCA10</sub>	93,7	3,0	5391	91	2,65	0,12
PL <sub>BTCA18</sub>	73,6	11,8	4896	200	2,46	0,20

**Impact test**

	Charpy (KJ/m <sup>2</sup> )	sd
P <sub>BTCA</sub>	11,4	1,7
P <sub>BTCA225</sub>	10,6	0,5
P <sub>BTCA10</sub>	14,8	0,2
P <sub>BTCA18</sub>	14,7	0,9
S <sub>BTCA</sub>	5,2	1,2
S <sub>BTCA225</sub>	6,1	0,3
S <sub>BTCA10</sub>	6,5	0,6
S <sub>BTCA18</sub>	7,0	1,0
PL <sub>BTCA</sub>	11,5	1,9
PL <sub>BTCA225</sub>	12,2	1,7
PL <sub>BTCA10</sub>	15,3	0,3
PL <sub>BTCA18</sub>	15,5	0,1

**Annex 1.2.** Numerical results of the mechanical properties of the composites reinforced with the fibres submitted by STFI.