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Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D5.22. Report on the preliminary characterisation of the first composite samples delivered in WP5.2 (month 18)

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PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
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CO	Confidential, only for members of the consortium (including the Commission Services)	

Revision: 0

WP 5.3 Material characterisation and testing

D5.22. Report on the preliminary characterisation of the first composite samples delivered in WP5.2

1.1.1 Objective

The objective of this deliverable is to report on properties of the first PLLA/cellulose fibre composites produced within WP5.2.

Characterisation of the first composite samples produced in WP5.2

The interaction with water either free water or moisture is one of the most important properties of a composite made using bio fibres. The reason for this is that bio-fibres can take up substantial amounts of water which leads to dimensional change.

Interaction with water

The water uptake was measured as weight gain of sample pieces left after mechanical testing. The samples were first dried at 40°C for 10 days. Samples were immersed in deionised water and kept at 20°C in closed containers. Before weighing samples were wiped and let to dry for three minutes.

Interaction with moisture

The moisture uptake was measured as weight gain of sample pieces left over after mechanical testing. The samples were first dried at 40°C for 10 days. Samples were placed in a small climate chamber holding 97 %RH (21°C), see also deliverable 5.20. The chamber was purged with nitrogen in order to decrease the risk for micro-biological activity. Sample weights were immediately determined after they had been taken out of the climate chamber.

Based on detected weight gains saturation points were calculated using the solver function in Microsoft excel. Measured weight gains were fitted to an empirical solution of Fick's second law.

Results

All samples except NPF6 contained 30 wt% fibres. The NPF6 sample contained 30 wt% fibres that contained 18% TiO₂. Re-calculating the composition the sample NPF6 contain 24,6% fibers, 5,4% TiO₂ and 70% PLLA. In the calculation of the fibre saturation point it has been assumed that TiO₂ does not take up any water.

Table 1. Water uptake of tested samples (weight gain in % of dry sample).

time (h)	PLLA	EPFG				Aveiro		Oulu		
		reference	MF2	MF3	MF4	reference	NPF6	DRF7	DRF8	DRF9
0	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
26	0,28	0,65	0,65	0,75	0,65	0,64	0,42	0,83	0,71	0,70
98	0,50	1,27	1,30	1,45	1,25	1,29	0,83	1,66	1,42	1,41
258	0,65	2,04	2,11	2,35	1,98	2,18	1,34	2,78	2,39	2,34
454	0,68	2,46	2,58	2,84	2,41	2,85	1,65	3,57	3,05	2,96
743	0,94	2,79	3,04	3,38	2,78	3,42	2,01	4,41	3,72	3,61
1026	0,71	2,95	3,26	3,62	2,96	3,66	2,20	4,72	3,87	3,76

In table 1 and 2 the measured weight gain under wet and moist conditions are given and in table 3 calculated saturation points are listed. All material took up water rather slowly probably because the uptake largely is controlled by diffusion rather than percolation. The PLLA took up 0,7 wt% water both in water and under moist conditions. Untreated fibres typically take up about 20-30 wt% water at 97 %RH. Of the tested materials no sample took up more than about 11,5 wt% suggesting that the fibres are prevented from swelling in the composite. It is also interesting to note the dramatically lowered water uptake of avicell. The avicell in the reference sample from France had a saturation point of about 8 that should be compared to e.g. DRF8 and 9.

Table 2. Moisture uptake of tested samples (weight gain in % of dry sample).

time (h)	PLLA	EPFG				Aveiro		Oulu		
		reference	MF2	MF3	MF4	reference	NPF6	DRF7	DRF8	DRF9
0	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
98	0,49	1,15	1,05	1,21	1,07	1,06	0,79	1,27	1,16	1,11
258	0,62	1,94	1,61	1,90	1,72	1,73	1,30	2,15	1,90	1,87
454	0,72	2,16	1,95	2,32	2,12	2,20	1,64	2,75	2,40	2,38
762	0,70	2,50	2,34	2,77	2,50	2,74	2,09	3,57	2,97	2,94
1026	0,71	2,53	2,37	2,82	2,55	2,82	2,21	3,75	3,04	3,03

A low water uptake should be regarded as positive and of the tested samples lowest water uptake was observed for the TiO₂ treated fibre composite NPF6. The fibre saturation point was in this case lowered from about 11 wt% for untreated sample to 5,9 wt%. Interesting to note is that the fibre saturation point under wet and moist conditions was the same for this sample. The chemically treated samples MF2-4 did not show any improved stability toward moisture or water. Instead a rather significant increase in both water and moisture fibre saturation points was observed.

Table 3. Calculated saturation points.

	comment	C _c (%) wet	C _f (%) wet	C _c (%) moist	C _f (%) moist
PLLA		0,69	-	0,71	-
reference	EFPG	2,88	7,99	2,53	6,78
	MF2	3,21	9,09	2,37	6,24
	MF3	3,56	10,26	2,90	8,01
	MF4	3,02	8,46	2,61	7,04
reference	Aveiro	3,77	10,96	2,94	8,14
	NPF6	2,26	5,92	2,28	5,94
	DRF7	4,83	14,49	3,90	11,34
	DRF8	3,97	11,62	3,15	8,84
	DRF9	3,92	11,46	3,15	8,84

Mechanical properties study

All the composites prepared by the research group of the University of Girona (UdG) were analyzed under different mechanical conditions: tensile, flexural and impact. The tensile and flexural tests were carried out in a Universal Testing Machine MTS (model 488) under the following conditions:

Table 4. Applied conditions in the evaluation of tensile and flexural mechanical properties.

Conditions	Tensile test	Flexural test
Temperature (°C)	23	23
Humidity(5)	50	50
Speed (mm·min ⁻¹)	46	1.4

The impact test was developed in a Charpy tester to obtain the need energy to break a sample of the material by the impact of a device by the action of the gravity.

The evaluated materials were based on PLLA as polymer matrix and different fibres, modified and non-modified, provided by other groups participating in the Sustainpack project. The composites as well as the different fibres used in this study are summarised in table 5.

Table 5. Fibres used for the preparation of PLLA-based composites.

Reference	Fibrous reinforcement	Reinforcement
P _{PLLA}	PLLA pure	0 %
C _{EFPG1}	AVICELL original (EFPG)	30 %
C _{EFPGMF2}	AVICELL modified PMDA_Av (EFPG)	
C _{EFPGMF3}	AVICELL modified BPTCDA_Av (EFPG)	
C _{EFPGMF4}	AVICELL modified PPDI_Av (EFPG)	
C _{AVEIRO5}	Fibres originals (AVEIRO)	
C _{AVEIRONPF6}	Fibres modified with nanoparticles TiO ₂ (AVEIRO)	
C _{OULUDRF7}	Dry refined CTMP (OULU)	
C _{OULUDRF8}	Dry refined mix of bleached softwood and hardwood kraft (OULU)	
C _{OULUDRF9}	Dry refined Bleached softwood kraft (OULU)	

Results

The values of the tensile mechanical properties are summarised in table 6.

Table 6. Mechanical properties of the prepared composites under tensile conditions.

Material	E-modul [GPa]	Stdev	Max stress [MPa]	Stdev	Strain [%]	Stdev
P_PLLA	3,58	0,05	69,14	0,63	2,44	0,04
C_aveiro_5	6,29	0,05	67,03	1,66	1,52	0,09
C_aveiro_NPF6	5,43	0,18	59,81	0,57	1,49	0,07
C_efpg1	5,41	0,04	56,61	0,28	1,38	0,03
C_efpg_MF2	5,88	0,10	60,58	0,23	1,47	0,03
C_efpg_MF3	5,61	0,04	52,46	0,70	1,27	0,02
C_efpg_MF4	5,50	0,07	52,45	0,14	1,28	0,03
C_oulu_DRF7	6,45	0,01	77,90	3,86	1,82	0,25
C_oulu_DRF8	6,33	0,02	74,42	2,33	1,87	0,26
C_oulu_DRF9	6,18	0,07	62,56	5,98	1,31	0,20

In the figure 1 the trend of the values of the Young Modulus, collected in table 6, is showed.

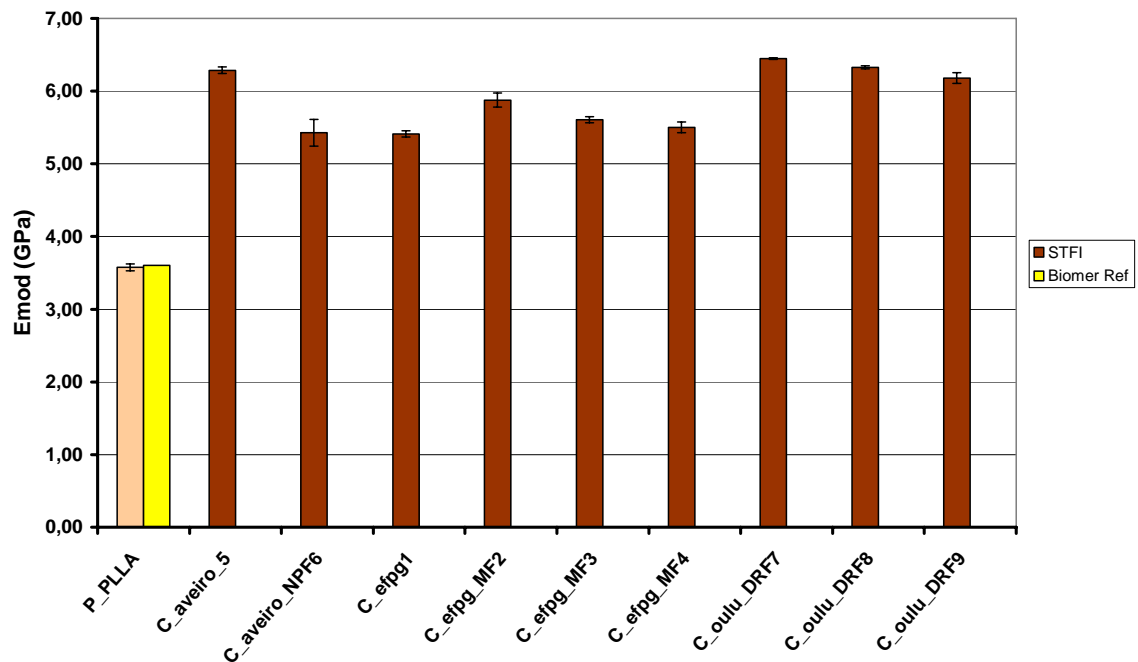


Figure 1. Values of the Young Modulus of the samples of composite.

All of the materials show a significant increase in this value, compared with the value assigned to the raw PLLA. This increase is the common answer of the reinforced materials. The efforts are transferred from the polymer matrix to the fiber, increasing the stiffness of the material. Considering the modification of the fibres, just the case of the modifications made by the group of the EFPG showed an increase of the Young Modulus, compared with the original fibre. In the case of the composites modified with the fibres obtained by the University of Oulu the three fibres produce a significant increase in the Young Modulus, but without high differences between themselves. It means that the stiffness related with the reinforcement is analogous for the three different modifications. In the particular case of the fibres modified with nanoparticles of TiO_2 , prepared by the group of the University of Aveiro, this modifications leads to a significant decrease of the Young Modulus.

In the figure 2 the trend of the values of the max stress, collected in table 6, is showed.

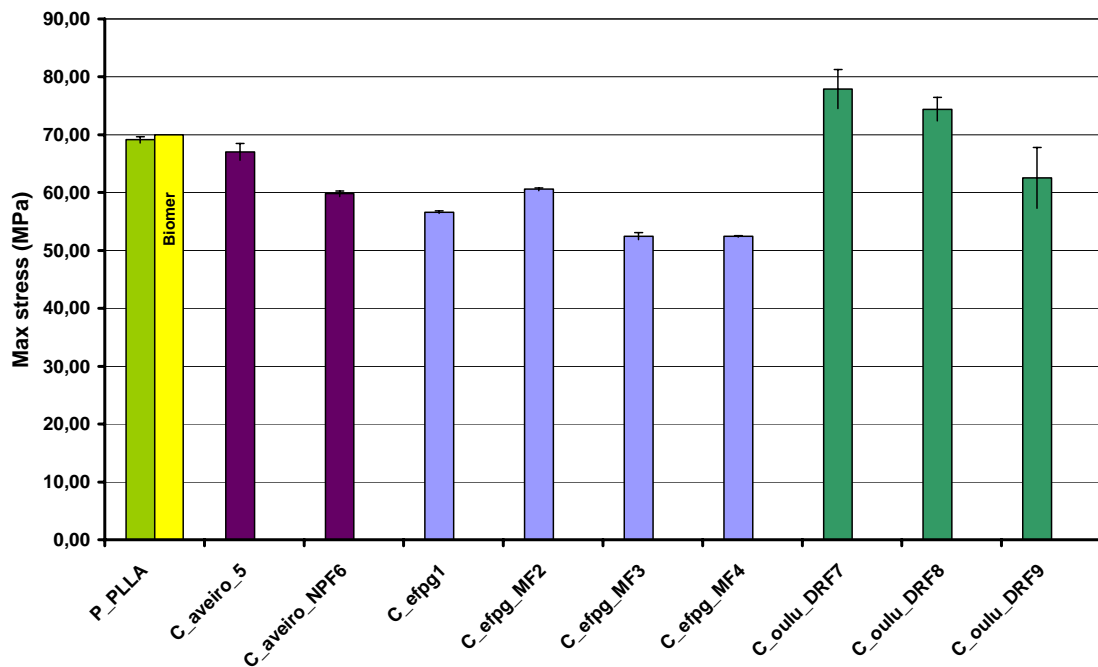


Figure 2. Values of the Max Stress of the samples of composite.

We can observe that all of the prepared composites showed a decrease in this property except for the materials reinforced with the dry refined fiber of the University of Oulu. In the other cases, the original fibres as well as the surface modified fibers, produced a decrease in the max stress. This result can be attributed to the presence of negative interface effects between both phases, the matrix and the reinforcement. This effect leads to a bad adhesion between both components.

The formulations of the composites suffered a significant decrease of the strain value as it can be observed in table 6. This result is consequent with an increase in the stiffness of the material where the composite loses the ability to be deformed under low loads due to the presence of the fibers in the structure.

The values of the flexural mechanical properties are summarised in table 7.

Table 7. Mechanical properties of the prepared composites under flexural conditions.

Material	E-modul [GPa]	Sdev
P_PLLA	3,00	0,06
C_aveiro_5	5,46	0,09
C_aveiro_NPF6	4,75	0,08
C_efpg1	4,59	0,10
C_efpg_MF2	4,80	0,19
C_efpg_MF3	4,61	0,08
C_efpg_MF4	4,67	0,09
C_oulu_DRF7	5,56	0,09
C_oulu_DRF8	5,45	0,05
C_oulu_DRF9	5,40	0,12

In all of the studied formulations a significant increase in the flexural modulus is observed. It is the same result obtained like in the case of the tensile test, so this increase is related to the increase in the stiffness of the material due to an effect of reinforcement.

Finally the results obtained in the impact test are summarised in table 8.

Table 8. Impact strengths for the composites based on PLLA and modified and non-modified fibers.

	Impact strength (KJ/m²)	Stdev
P_PLLA	33,5	16,19
C_aveiro_5	14,06	0,63
C_aveiro_NPF6	17,2	1,31
C_efpg1	13,44	1,77
C_efpg_MF2	15,91	1,28
C_efpg_MF3	12,86	0,62
C_efpg_MF4	13,91	1,27
C_oulu_DRF7	23,35	1,96
C_oulu_DRF8	20,37	1,39
C_oulu_DRF9	17,22	0,97

All the composites lose the ability to absorb the energy of the impact due to the increase in the stiffness of the material. The compositions have less amount of polymer matrix which is the viscoelastic component of the composite. Due to the lower stiffness of the polymer matrix compared with the reinforced materials this matrix is the component that has a major capacity to dissipate the impact energy. Because of this decrease in the amount of the viscoelastic component in the composite the needed energy to break the samples decreases.