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Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

Deliverable 5.29

Report on the selected ways of modifying the fibres by preparing inorganic nanoparticles / hybrids cellulose fibres to make them suitable for the preparation of 3D thermoplastic composites

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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)	

SUSTAINPACK

WP5.1. – Fibre Modification

Deliverable 5.29

Report on the selected ways of modifying the fibres by preparing inorganic nanoparticles / hybrids cellulose fibres to make them suitable for the preparation of 3D thermoplastic composites

1. Composites preparation (UAVR, in collaboration with EFPG)

Hybrids of cellulose with titanium dioxide, calcium carbonate and silica were prepared following the optimized methodologies already described in previous deliverables. Generally, the methodologies involve the in situ synthesis of the inorganic phase in the presence of cellulose fibres or the layer by layer (LbL) procedure using polyelectrolytes to mediate the connection between the previously precipitated inorganic particles and cellulose fibres.

The selected polymer for the composites preparation was commercial biodegradable polyester Mater-Bi.

The composites were prepared using a DSM microcompounder (microextruder). The hybrids and the polymer were mixed at 90 °C during selected time considered adequate for a homogeneous mixture. The extracted composites were then pressed using a uniaxial Hot-press. Although the best operating conditions for the composites preparation were chosen, some of final composites showed some structural heterogeneity assigned to an incomplete dispersion of the fibres in the polymer matrix. The compositions of the composites are described in the table.

Table - Composition of the composites

Inorganic phase		Preparation method	Inorganic content in the fibres (% w/w)	% of hybrid or blank fibre in the composite (w/w)
none	B1	blank	-	20
	B2	blank	-	30
	B3	Fibre treated with polyelectrolytes (LbL)	-	30
TiO ₂	T1	In situ	19	20
	T2	In situ	14	20
	T3	LbL	9	20
	T4	LbL	11	20
CaCO ₃	C1	In situ	8	30
	C2	LbL	6	30
	C3	LbL	7	30
	C4	LbL	10	30
	C5	LbL	16	30
SiO ₂	S1	In situ	25	20
	S2	LbL	5	20
	S3	LbL	7.5	20
	S4	LbL	10	20

2. Composites characterization

The composites were tested by dynamical mechanical analysis (at EFPG, Grenoble) and water absorption studies (UAVR).

2.1. Water absorption studies (UAVR)

The composites were completely immersed in distilled water as shown in Figure 1. To determine the water uptake ability, composites were removed from water, cleaned with absorbent paper, weight and re-immersed in water, during regular times.



Figure 1 – Picture of the composites specimens immersed in water.

The values of the water absorption are graphically represented in Figures 2-4.

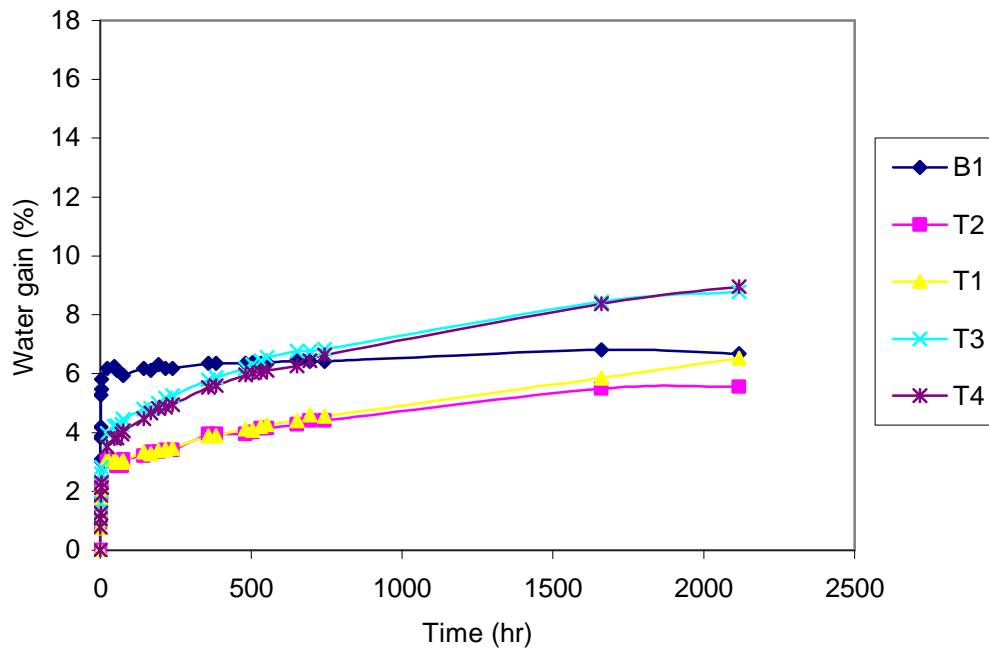


Figure 2 – Curves of weight gain due to water absorption by the composites prepared with 20% (w/w) of TiO_2 /cellulose in comparison with the composite prepared with 20% of blank fibres.

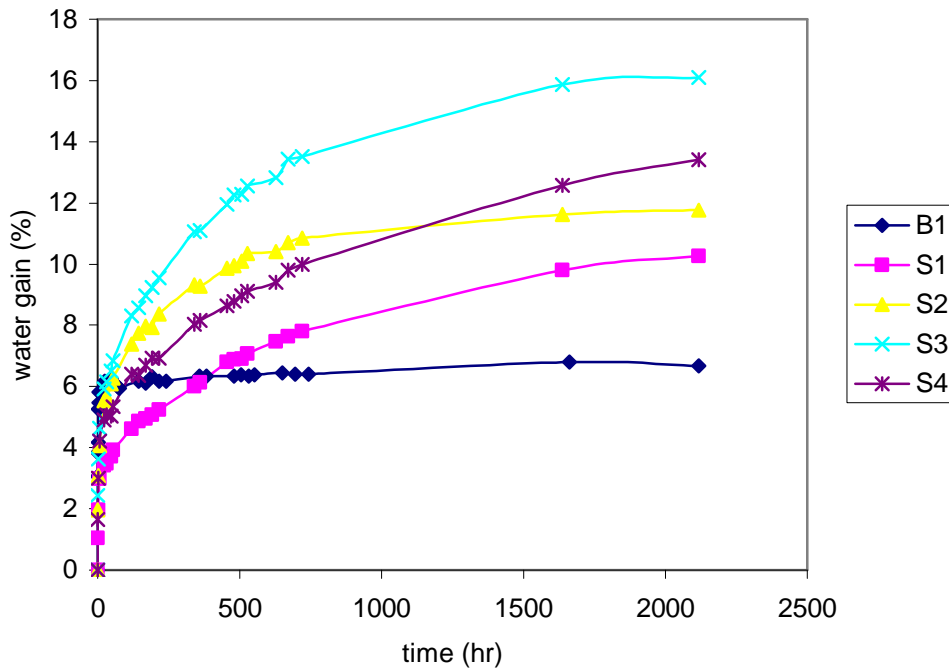


Figure 3 – Curves of weight gain due to water absorption by the composites prepared with 20% (w/w) of SiO_2 /cellulose in comparison with the composite prepared with 20% of blank fibres.

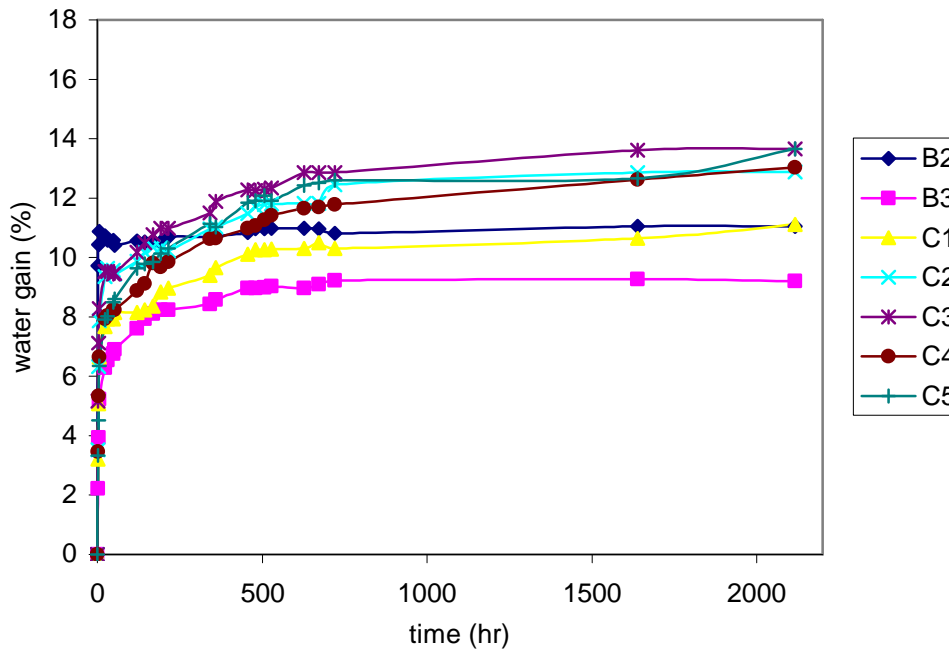


Figure 4 – Curves of weight gain due to water absorption by the composites prepared with 30% (w/w) of CaCO_3 /cellulose in comparison with the composites prepared with 30% of blank fibres and 30% of fibres treated with polyelectrolytes.

From the results obtained, some tendencies can be outlined:

- Generally, the composites prepared with hybrids synthesised *in situ* confer less ability for water uptake than the composites prepared with hybrids obtained from the LbL approach;
- For some hybrids, the deposition of inorganic particles onto fibres, retard the penetration of water in the early stages (250-750 h) of immersion of composites in water but, later, the uptake of water increases with respect to blank fibres.
- The water uptake increases with the fibre load (comparison between B1 and B2). For the same load, the treatment of the fibre with polyelectrolytes (without mineral particles) decrease the water uptake (comparison between B2 and B3);
- During the period studied, the composites prepared from TiO₂/cellulose hybrids synthesized *in situ* are the unique that absorb less water than the equivalent blank composite.
- The composites prepared with SiO₂/cellulose fibres, particularly those prepared by the LbL approach, present the higher percentage of water uptake;

2.2 – DMA analysis (EFPG)

DMA characterization was done in the same conditions for all the composites. Each composition was tested more than two times in order to achieve reproducible results. The results are plotted in the next figures where the elastic modulus (E') is represented as a function of temperature. The curve of the polymer without fibres (B0) was plotted in all figures for comparison.

The mechanical reinforcement due to the fibres incorporation in the polymer matrix is observed when compared to blank polymer. Composites prepared with 30% of reinforcement are denser than composites prepared with 20%, conferring higher interaction between fibres and the mechanical properties are superior.

Generally, composites prepared with hybrids with higher content of inorganic phase present lower mechanical properties. Probably, the presence of inorganic particles at fibres surface hinders the inter-fibre and fibre-polymer interactions.

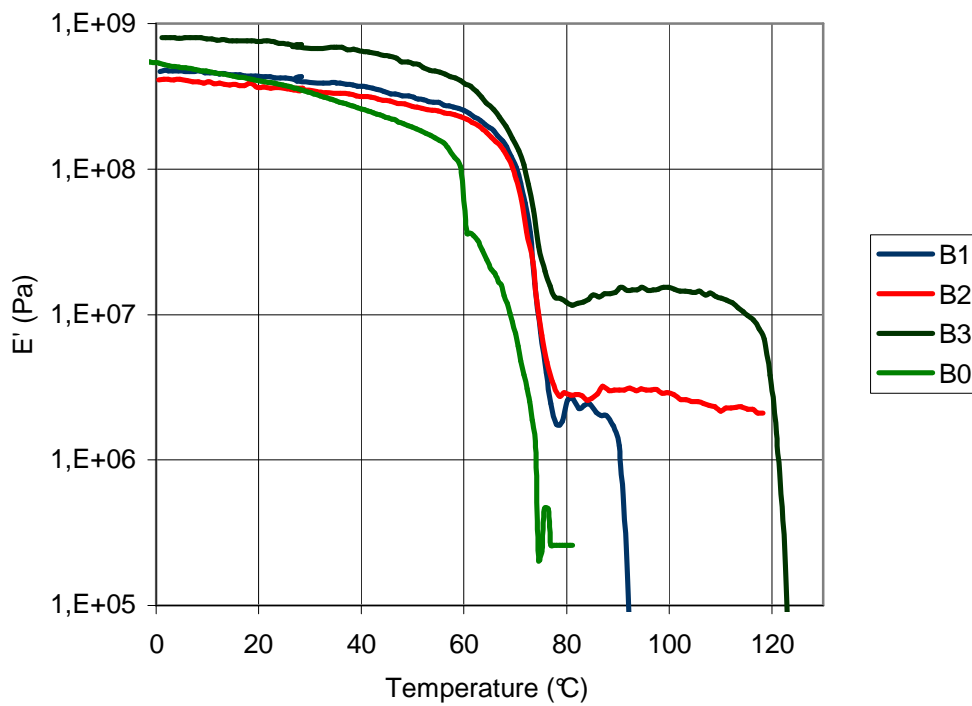


Figure 5. Elastic modulus in function of temperature for blank composites.

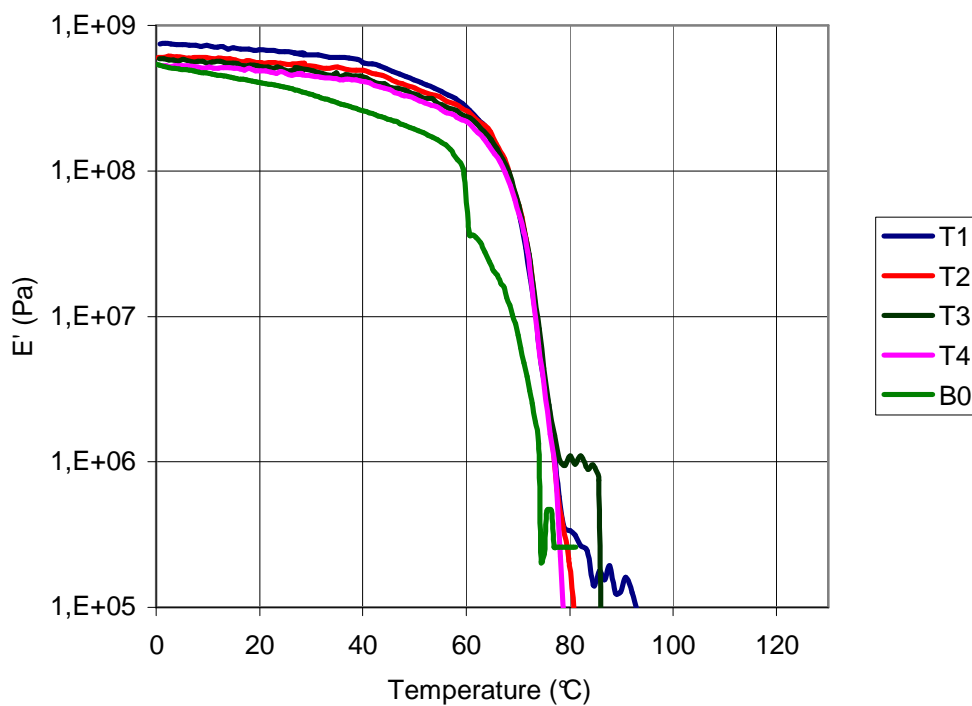


Figure 6. Elastic modulus in function of temperature for composites prepared with TiO_2 /cellulose hybrids.

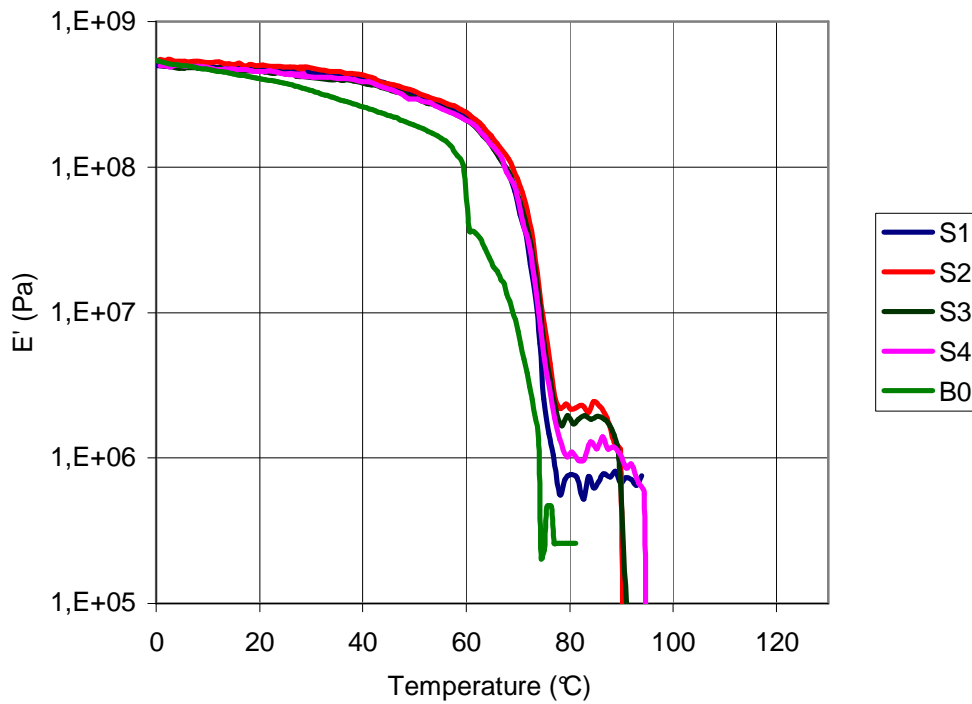


Figure 7. Elastic modulus in function of temperature for composites prepared with SiO₂/cellulose hybrids.

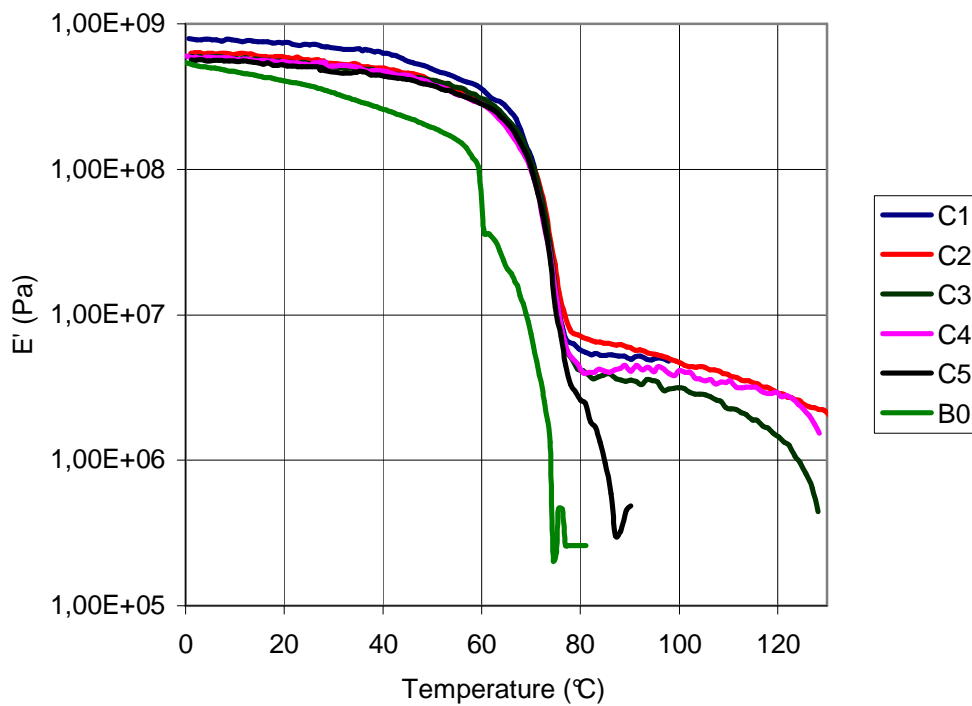


Figure 8. Elastic modulus in function of temperature for composites prepared with CaCO₃/cellulose hybrids.

3. Conclusions

Composites were prepared from inorganic nanoparticles/cellulose hybrids and commercial polyester MaterBi.

Composites prepared with hybrids synthesised *in situ* confer less ability for water uptake than the composites prepared with hybrids obtained from the LbL approach, thus increasing the dimensional stability in wet environments.

During the period studied, the composites prepared from TiO₂/cellulose hybrids synthesized *in situ* absorbed less water than the other hybrids and than the equivalent blank composites.

Generally, composites show better mechanical properties than the polymer itself due to fibre load, but the increase of particles load at fibre surface show an opposite effect.