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Sustainpack
Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D5.17A – Report on recycling ability of biodegradable matrices in the plastic recycling stream

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UNIVERSITAT DE GIRONA (UdG)
ÉCOLE FRANÇAISE DE PAPETERIE ET DES INDUSTRIES GRAPHIQUES (EFPG)

WP5.3

REPORT ON RECYCLING ABILITY OF BIODEGRADABLE MATRICES IN THE PLASTIC RECYCLING STREAM

Objective

The objective of this deliverable is to report the results related with the ability of biodegradable matrices to be recycled in the plastic recycling stream before to analyse this ability to fibre reinforced composites.

The biopolymers tested are: PLLA, Polyester Mater-Bi and Starch based Mater-Bi biopolymer.

PLLA Poly(L-Lactide) biopolymer

This biopolymer has been moulded by injection in a temperature range of 175-195ºC. The maximum number of cycles tested was 8. The mechanical properties of the different samples obtained decrease dramatically as it will be showed.
In figures 1 and 2, tensile strength and elongation at break are represented in function of cycles. These properties decreased smoothly after 5 recycling processes, but in the sixth the decrease was very acute. After the fifth cycle, a low temperature (150 ºC) must be used to process the material.

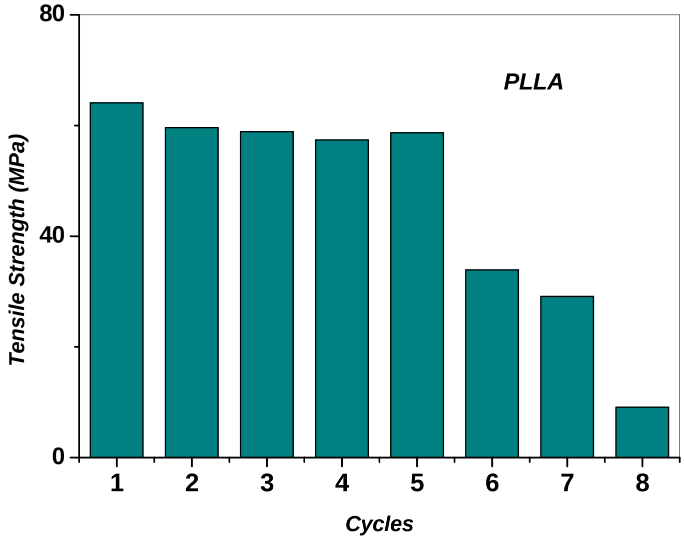

Figure 1: Tensile strength versus the process cycles for PLLA biopolymer.

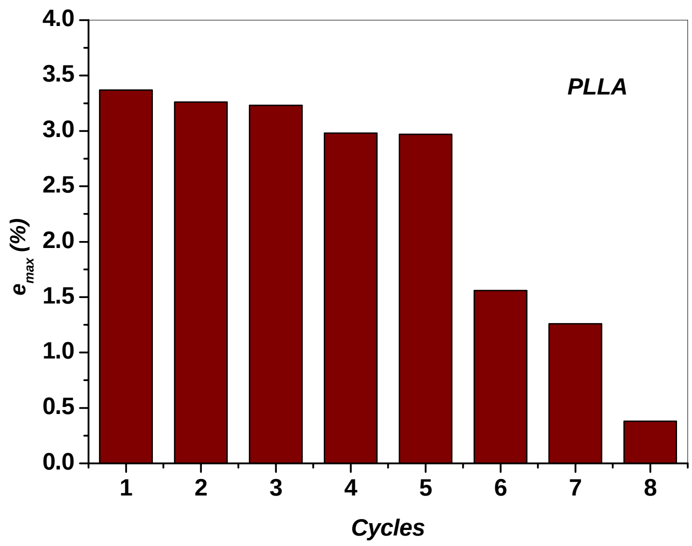

Figure 2: Elongation of PLLA in function of different reprocessing cycles.

On the other hand the Young Modulus didn't suffer changes with increasing the processing cycles as can be seen in Figure 3.

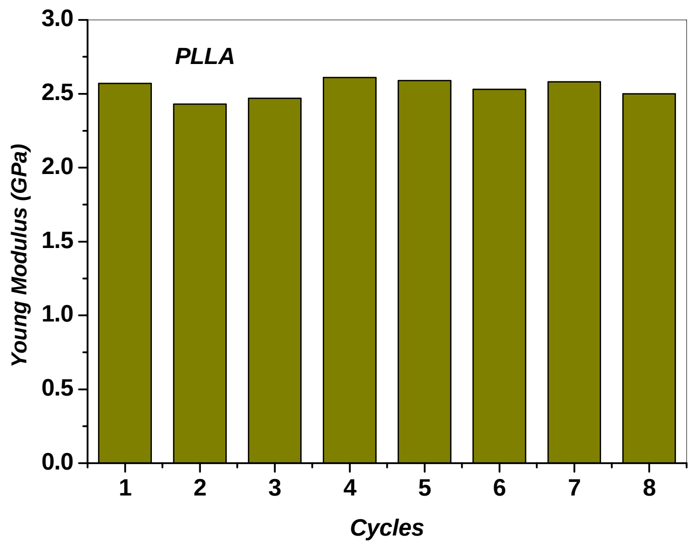

Figure 3: Influence of reprocessing PLLA on the Young Modulus property.

The tensile energy absorption decreased progressively with the increase of process cycles, being this effect drastically significant after the fifth cycle as shown in figure 4.

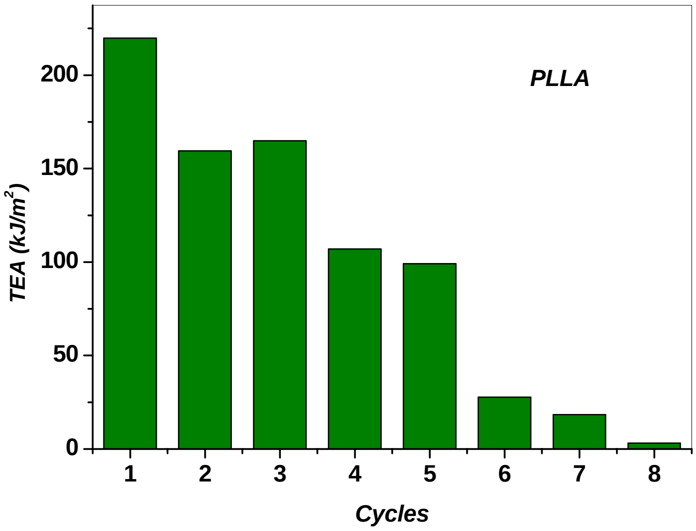

Figure 4: Evolution of TEA versus the process cycles of PLLA.

The flexural strength and the flexural elongation followed a similar trend to that of tensile properties, as it is showed in figures 5 and 6. Regarding flexural modulus, any relevant change was observed (Figure 7).

Concerning to the Izod impact test, the results are showed in Figure 8. A significant decreasing was observed after the fifth cycle.

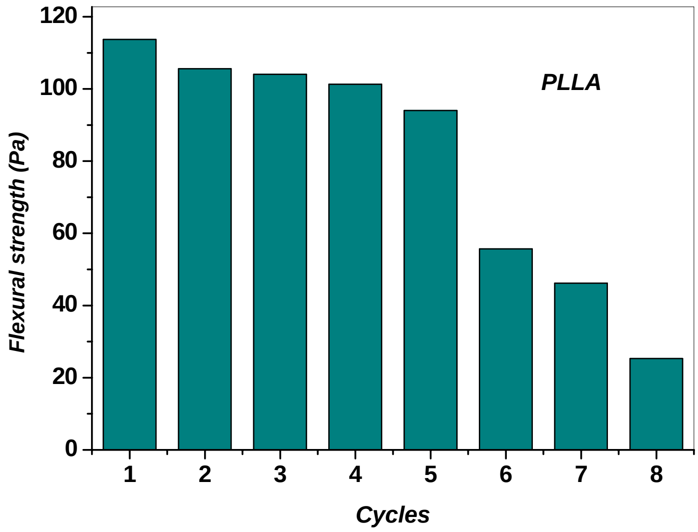

Figure 5: Flexural strength versus the process cycles using PLLA.

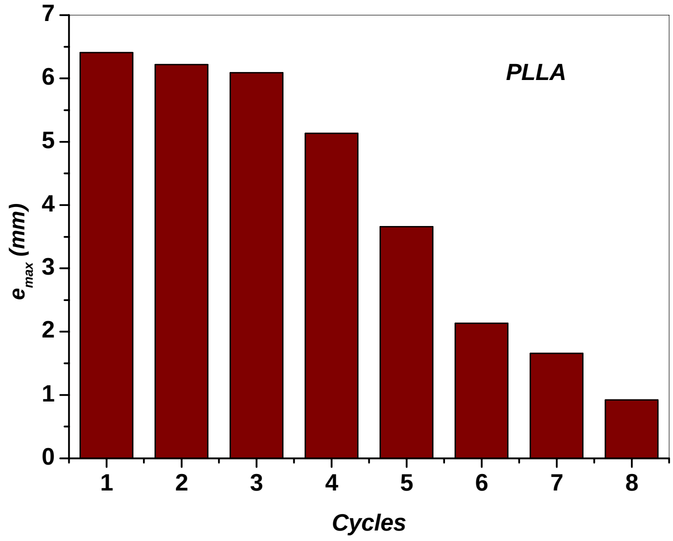

Figure 6: Flexural elongation versus the process cycles using PLLA.

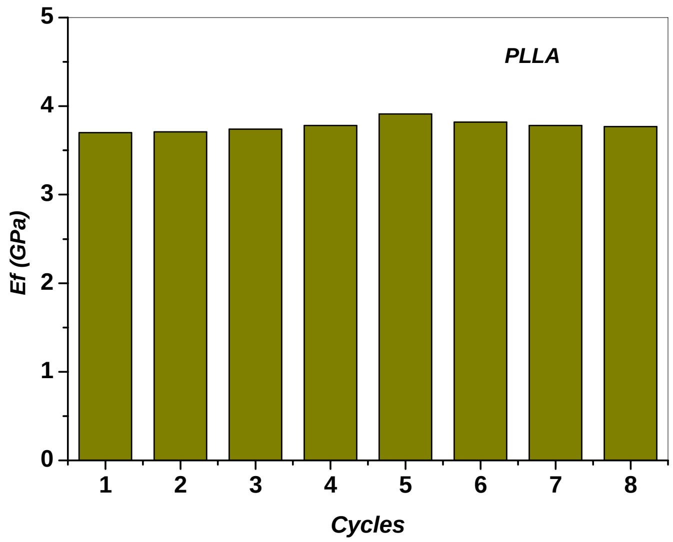

Figure 7: Flexural modulus versus the process cycles using PLLA.

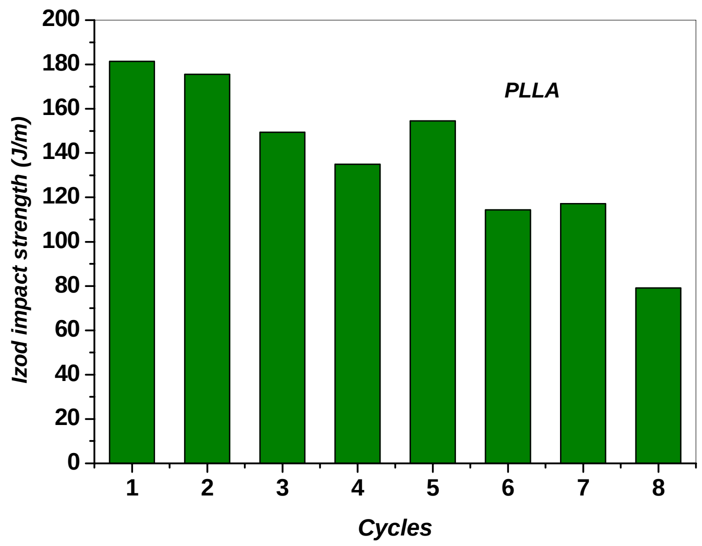

Figure 8: Izod impact strength versus process cycles using PLLA.

In addition to mechanical properties, melt flow index fort he material obtained in each recycling process has been obtained. As it is observed in figure 9, MFI increased with the process cycles only after the first cycle, from where the increasing was lineally.

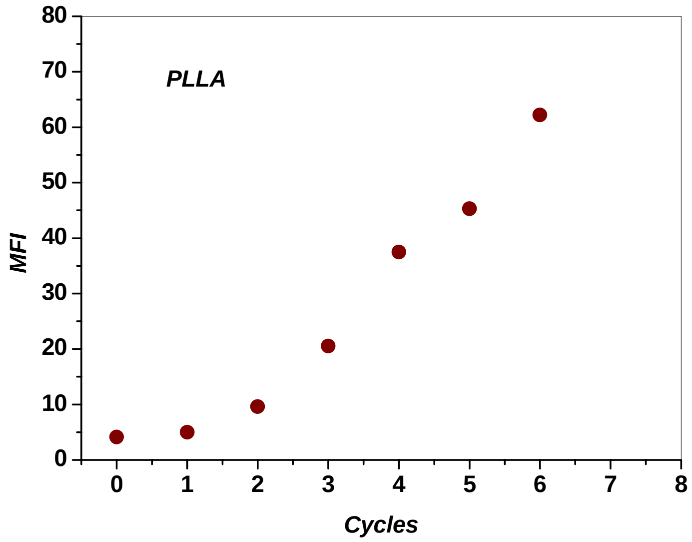

Figure 9: Values of Melt Flow Index versus process cycles using PLLA.

Gel permeation chromatography (GPC) has been performed for the evaluation of the biopolymer molecular weight. Two different values have been obtained: Mw and Mn.

Mw is the average molecular weight in weight (Dalton)

Mn is the average molecular weight in number (Dalton)

These molecular weights are referred to polystyrene as internal standard.

As it is showed in figure 10, due to reprocessing of the material the molecular weight of the polymer decreased. The Mn (average molecular weight in number) corresponding to 8 completed cycles decreased about 80 %.

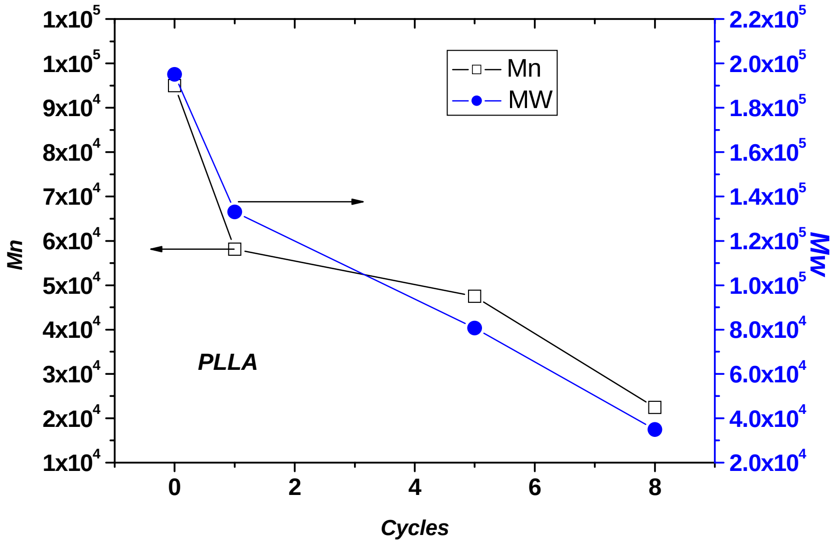

Figure 10: Evolution of molecular weight obtained by GPC in function of recycling cycles.

Another technique applied to the characterisation of recycling ability of biopolymers to be introduced in plastic recycling stream is Differential Scanning Calorimetry (DSC).

Figure 11 shows the DSC evolution with the number of injection cycles. For all specimens the Tg temperature has close values. But it seems a smooth decreasing if the number of cycles increases. A decrease in the melting temperature is observed when increasing the number of cycles due to a decreasing in the molecular weight of the polymer.

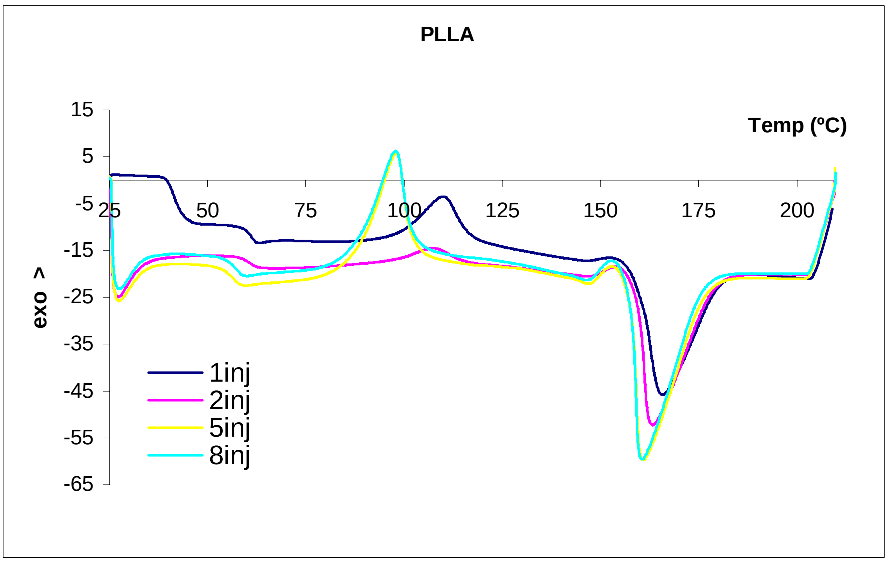

Figure 11: DSC values for PLLA at several process cycles.

At last, Thermogravimetric Analysis (TGA) were also evaluated. Results obtained are presented in figure 12.
The evolution of the degradation process is similar in all the cases, but the process started at lower temperatures with the increase of processing cycles.

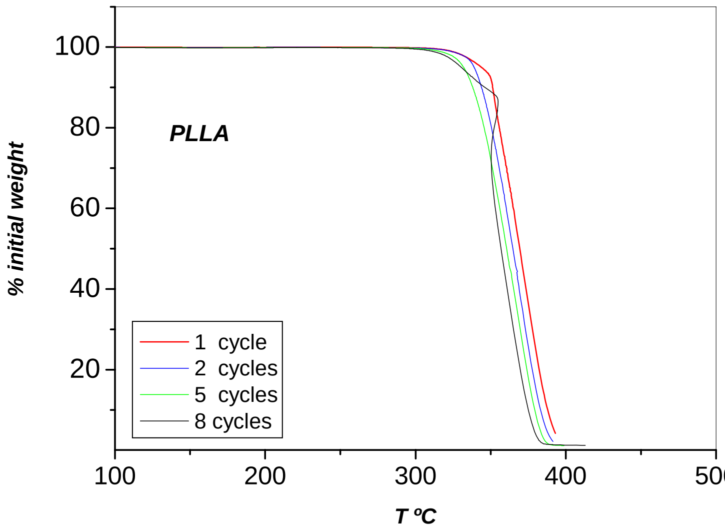

Figure 12: TGA curves for PLLA at different recycling cycles

As conclusion of the analysis of pLLA, it is important to notice that he mechanical behaviour decreased by increasing the number of cycles, being acuter after the fifth cycle. This is in agreement with the results of the MFI test which increases by increasing the number of cycles. The molecular weight decreased and that was confirmed by TGA and DSC analysis.

Polyester Mater-Bi

This biopolymer has been moulded each time by injection in a temperature range of 120-140 ºC. The maximum number of cycles tested was 10.

In table I to III, mechanical values obtained are presented.

Table I: Values of tensile strength, elongation at break, Young modulus and tensile energy adsorption for different recycling cycles using Polyester Mater-Bi.

Cycle	Tensile Strength (MPa)	sd	e.max (%)	sd	Young modulus (GPa)	sd	TEA (KJ/m2)	sd
1	22.0	0.2	16.67	0.27	0.48	0.02	515.9	4.7
5	21.7	0.3	16.99	0.58	0.48	0.02	510.6	5.9
10	21.7	0.1	17.34	0.81	0.45	0.02	509.4	5.1

Table II: Values of flexural strength, elongation at break ant flexural modulus for different recycling cycles using Polyester Mater-Bi.

cycle	Flexural Strenth (MPa)	sd	e.max (mm)	sd	Flexural modulus (GPa)	sd
1	24.9	0.2	12.09	0.72	0.44	0.01
5	24.9	0.2	11.64	0.27	0.45	0.01
10	23.8	0.2	11.89	0.39	0.43	0.01

Table III: Values of Izod impact test for different recycling cycles using Polyester Mater-Bi.

cycle	R. Izod (J/m)	sd
1	39.9	4.9
5	35.8	3.1
10	32.7	1.7

Analysing the mechanical properties for the different processing cycles, tables I, II and III, show no drastic decreasing in these properties, even keeping in mind that 10 cycles has been tested. The degradation of the material is obvious, but it can be recycled better. It should be observed that the processing temperature is lower.

The Melt Flow index analysis show that MFI increased with the number of cycles, but it was smaller compared to that of PLLA (figure 13).

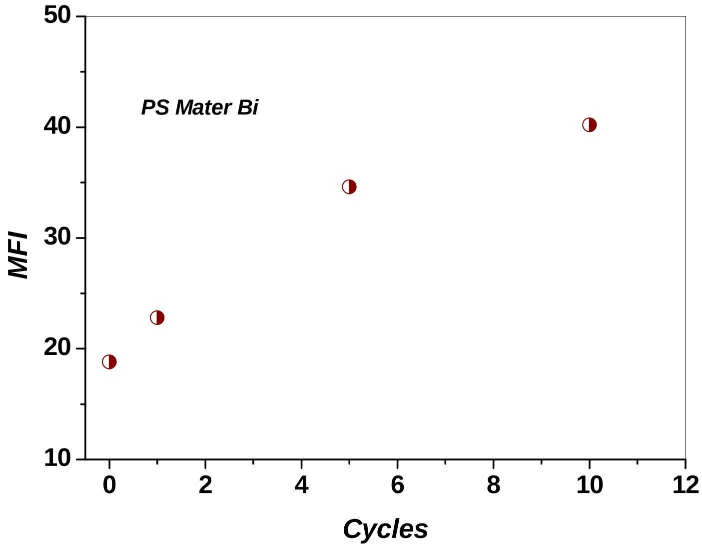

Figure 13: Melt Flow Index versus process cycles using Polyester Mater-Bi.

Gel permeation chromatography (GPC).

The gel permeation chromatography (GPC) whose values are presented in figure 14, showed a molecular weight decreases with the number of cycles but only reaching a 20% of initial values.

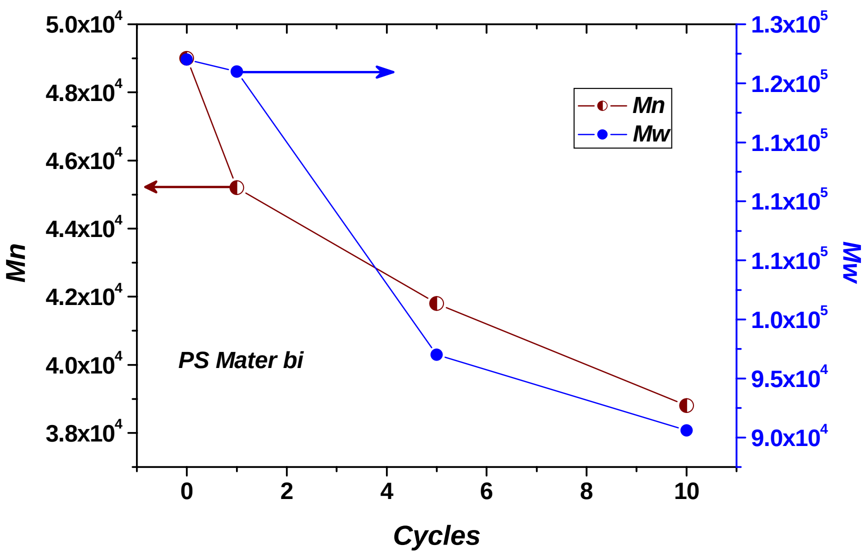

Figure 14: Values of Mn and MW obtained by means of GPC versus the number of cycles using Polyester Mater-Bi.

The Differential Scanning Calorimetry (DSC) technique gives us the results presented in figure 15. A smooth melting temperature decreasing was observed by increasing the number of cycles, but it can be considered that these variations are not significant.

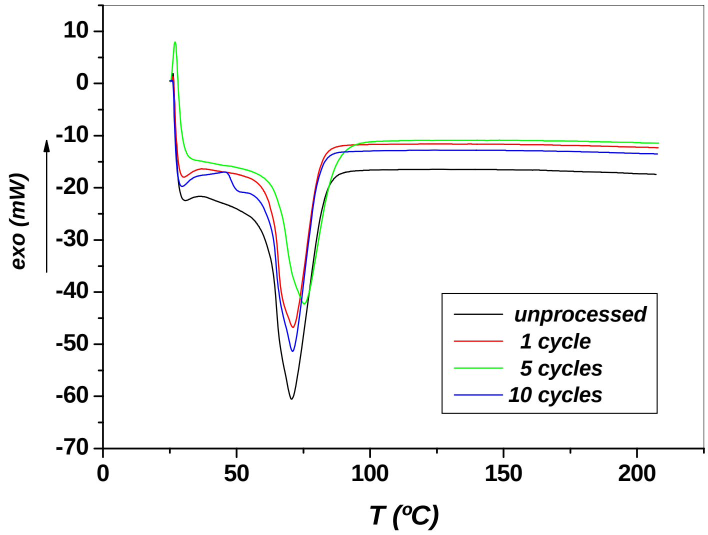

Figure 15: DSC curves for Polyester Mater Bi in function of different cycles.

The results obtained by TGA analysis on polyester Mater-Bi submitted to different processing cycles are presented in figure 16. A decrease of degradation temperature with the recycle was obtained, but as in the last DSC analysis, it is not considered significant.

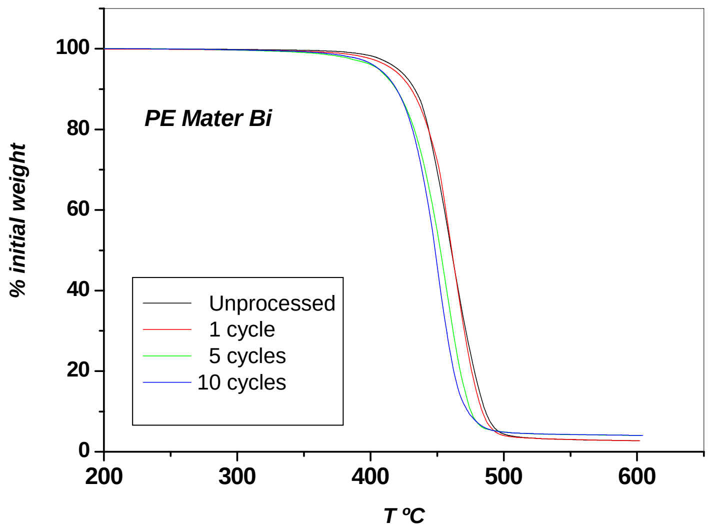

Figure 16: TGA curves for Polyester Mater Bi at several process cycles

As a conclusion it can be said that the degradation of the biopolymer Polyester Mater-Bi due to the recycling in the plastic stream process is not very significant. The mechanical properties decreased, but not so much. The decrease of the molecular weight was less than the observed by using PLLA as biopolymer.

Starch Mater Bi

This biopolymer has been moulded each time as the other polymers by injection. The maximum number of cycles tested was 2 because of the serious degradation of the plasticity properties of this biopolymer.

In table I to III, mechanical values obtained are presented.

Table I: Values of tensile strength, elongation at break, Young modulus and tensile energy adsorption for different recycling cycles using Starch Mater-Bi.

Cycle	Tensile Strength (MPa)	sd	e.max (%)	sd	Young Modulus (GPa)	sd	TEA (KJ/m2)	sd
1	29.2	0.4	2.27	0.22	2.05	0.15	78.0	10.1
2	32.1	0.8	2.39	0.17	2.13	0.16	73.0	7.4

Table II: Values of flexural strength, elongation at break ant flexural modulus for different recycling cycles using Starch Mater-Bi.

Cycle	Flexural Strendth (MPa)	sd	e.max (mm)	sd	Flexural Modulus (GPa)	sd
1	59.9	0.9	6.32	0.43	2.80	0.12
2	64.3	1.8	5.94	0.13	2.96	0.13

Table III: Values of Izod impact test for the recycling cycles using Starch Mater-Bi.

Cycle	R. Izod (J/m)	sd
1	18.6	2.1
2	20.1	3.4

Table IV: Values of MFI for the recycling process using Starch Mater-Bi.

Cycle	MFI (g/10 min)	sd
Unprocessed	9.2	0.8
1	16.7	1.2
2	16.5	0.8

Analysing the results presented it can be concluded that this biopolymer only can be processed one time. In the second cycle the material loses plasticity and can not be processed again.