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Rapport de recyclage des pièces ou rebuts industriels - Technical report on the recycling of industrial components and waste

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KAÏROS

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PP Leader : Kaïros

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Deliverable N° & name :

- **2.4.2 Rapport de recyclage des pièces ou rebuts industriels - Technical report on the recycling of industrial components and waste**

Content

1 Context of activity 2 – WPT2

In this activity Kaïros has developed new composite materials, of monolithic and sandwich structure using the non-woven preform of slightly oriented flax fibers, manufactured by Écotechnilin. These materials are intended for the development of a point-of-sale (POS) advertising medium. Consequently, their surface conditions must be smooth and without visible defects in order to respect the aesthetic challenges of this field of application. The environmental footprint of these new materials is reduced thanks to their high potential for recyclability and compostability and to biosourced raw materials. Kaïros must ensure that the materials meet the specifications imposed by the field of POS (machinability, aesthetic appearance, lightening, good mechanical strength) while checking that they have a good capacity for recycling. These materials are made using the thermocompression process which promotes a short manufacturing cycle time and a low cost of implementation. The purpose of this deliverable is to study the recyclability of these materials and to consider relevant end-of-life routes.

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1 Introduction

Recent concerns around climate change are forcing manufacturers to turn to more environmentally friendly solutions. This is particularly the case in the area of POS (Point of Sale Advertising) which generates nearly 100,000 tonnes of waste per year in France due in part to the short lifespan of its products. However, this waste is very little recycled or recovered since these materials are petro-sourced. In addition, the lack of a recovery channel and the cost of collection and treatment dissuade users from managing the end of life of their materials. However, regulations push companies to reduce emissions and recycle. Thus, alternatives to petro-based materials are emerging, such as bio-based and/or biodegradable composites composed of natural fibers and biopolymers.

Kaïros thus offers flax/PLA or hemp/PLA biocomposites in the form of plates for the POS field. PLA is the 2nd most produced bio-based and biodegradable polymer in the world with more than 217,000 tonnes per year. As for flax fibre, 2/3 of its production is made in Europe, making it a local material. In addition, its cost is affordable compared to synthetic fibers Among the many polymers reinforced with natural fibers, the combination of these two constituents has good mechanical properties

Concerned about its environmental impact, Kaïros wishes to offer more than its biosourced and biodegradable material, called Kairlin®. This company wants to set up its own recycling sector. One of the avenues for recovering this material is the use of Kairlin® plate scraps for implementation by injection. The life cycle analysis carried out by demonstrates that recycling remains the means of recovering biocomposite waste with the least impact on the environment. However, the mechanical properties deteriorate during the recycling process. Thus, recycled PLA must be mixed with virgin PLA in order to maintain acceptable mechanical properties.

The objective of the study is to determine whether the recycling of Kairlin® by injection is a possible way for the reuse of this waste in a new product.

2 Project progress

The project is carried out in partnership with UBS and will take place in 3 phases detailed in the action plan in figure 1.

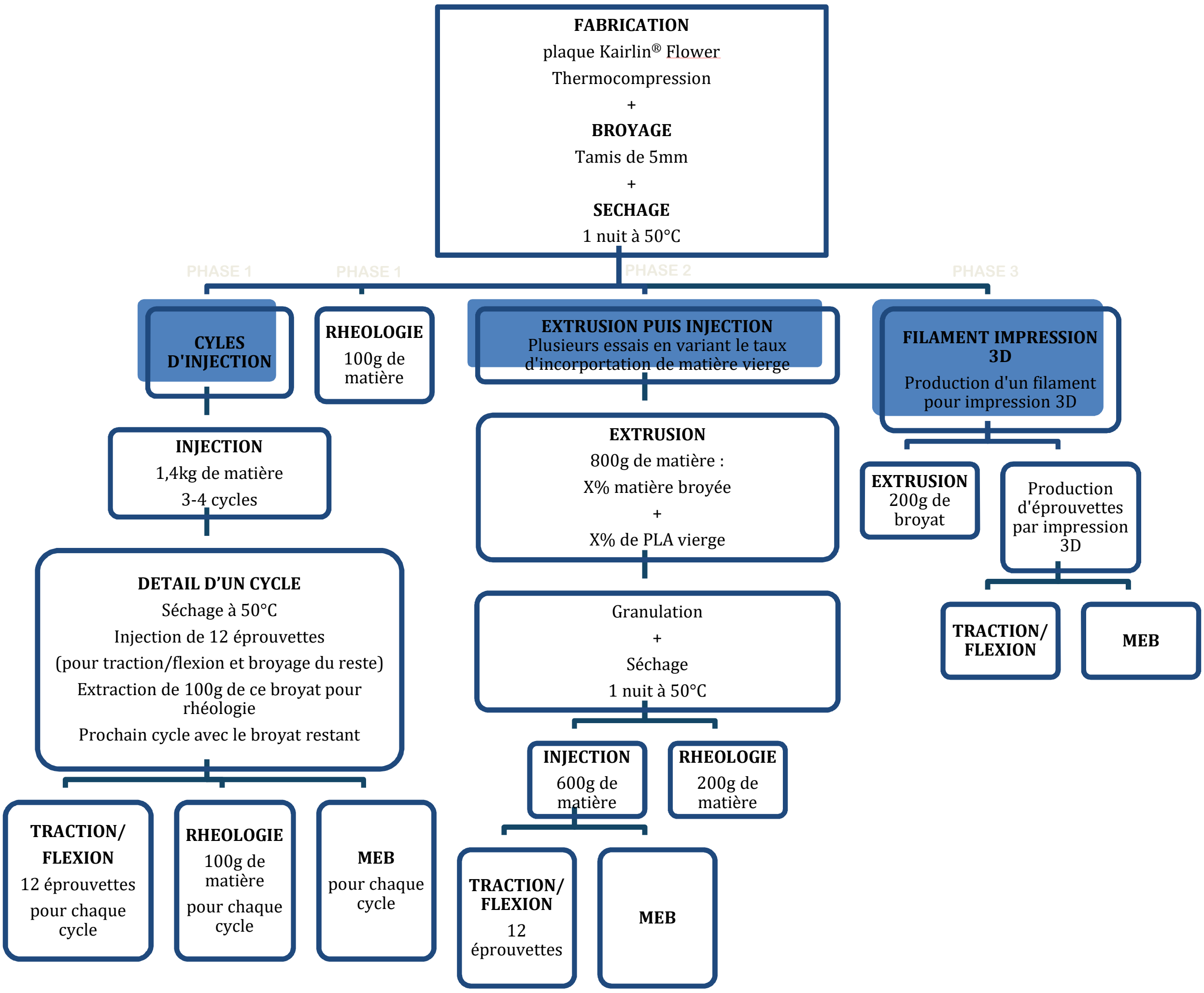


Figure 1 : Plan d'action

3 *Phase 1 : injection without extrusion*

The first phase consists of testing the simplest way of recycling. The shredded material is directly injected without first undergoing an extrusion step.

3.1 *Materials*

The monolithic Kairlin® used to constitute the shredded material is composed of:

- 2 layers of PLA film;
- 24 layers of Flower linen/PLA nonwoven.

3.1.1 Flower Non-woven flax/PLA

The preform is made of flax reinforcement combined with thermoplastic fibers of polylactic acid (PLA) by a needling process so that the fibers are slightly oriented in the direction of the unwinding of the reel. The proportion of flax in the preform is 40% while PLA constitutes 59.4%, carbon black dye accounts for the remaining percentage. The grammage of the nonwoven is equal to 100g/m2. This material presented in figure 2 is provided by Écotechnilin.

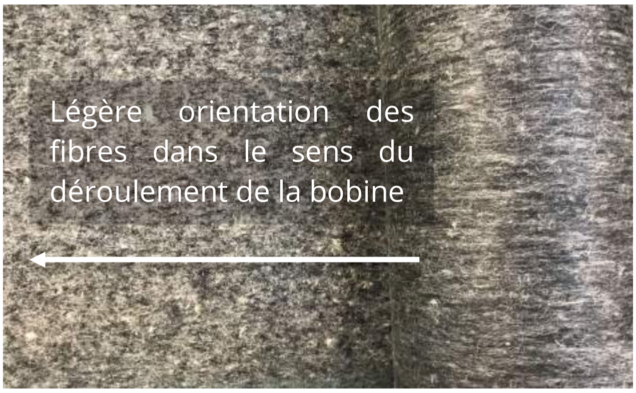


Figure 2 : préforme non tissée légèrement orientée dans le sens du déroulement de la bobine

3.1.2 PLA film

PLA films are added to the upper and lower surfaces of the composite plate in order to remedy surface porosity problems and obtain a more aesthetic surface finish. The film has a thickness of 350µm for a weight of 435g/m2. It is supplied by the Loparex company. The raw material comes from NatureWorks under the reference 4043D. This PLA has a density of 1.24g/m3, a melting temperature of 160°C, a maximum stress of 145MPa and a Young's modulus of 3.8GPa.

3.2 *Method*

3.2.1 Production of the plates

The assembly of the components of the monolithic plate is carried out by stacking the flax/PLA nonwovens and the PLA films following a stacking sequence. PLA films cover the outer faces of the final plate. The stacking sequence is depicted in figure 3.

Figure 3 : drapage des plaques destinées à être broyées

Once draped, the Kairlin® plates are made by thermocompression with a LAB Tech Scientific 50T hydraulic press. The temperature/pressure cycle is defined below:
- Preheating: bringing the sample into contact with the two platens of the press at a temperature of 200°C for 5 minutes;
- Hot pressing: a pressure of 20 bars is applied to the sample and to the block for 2 minutes, the temperature of the plates is always 200°C;
- Cooling: the assembly is moved to the cold platens of the press. Cooling takes place at 40° for 5 minutes.
This temperature/pressure cycle is shown in Figure 4

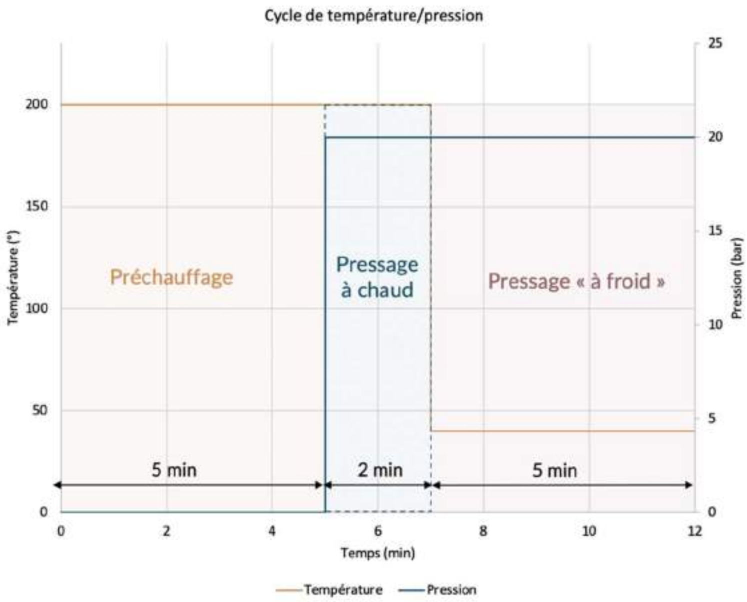


Figure 4 : cycle de température/compression

3.2.2 Grinding

The plates measuring 260 x 260 x 3 mm are crushed using a CMB knife crusher with a 5mm grid. These shredded materials constitute the raw material for the injection cycles, they are composed of 70.2% PLA, 29.4% flax fibers and 0.4% carbon black dye. No virgin material is added during this process.

3.2.3 *Injection process*

In order to assess the degradation of the material due to the recycling process, four injection cycles are carried out. For each cycle, 12 specimens are kept for mechanical tests while the others are crushed. Part of this ground material, 100g, is extracted for rheology tests. The injection press used is a Battenfeld HM 80/200 and the injection parameters are given in Table 1. The material is dried before injection in order to avoid the formation of steam and the degradation of the manufacture of the specimens.

Tableau 1 : paramètres d'injection pour les essais de la phase 1

Température du moule (°C)	Pression d’injection (bar)	Temps d’injection (s)	Température d’injection (°C)	Temps de refroidissement (s)
25	1600 - 1400 -1200 - 1000 - 0	9,6	190	20

3.2.4 *Mechanical trials*

Tensile and bending tests are carried out with an MTS Synergie RT/1000 equipped with a 10kN cell and an extensometer with a displacement length of 25mm. Concerning the tensile tests, the parameters are:

- Movement speed of 1mm/min;
- Useful length of the specimen: 60mm;
- Standard followed: ISO 527-2

The parameters chosen for the bending tests are:
- Movement speed of 2mm/min;
- Range: 64mm;
- Length of the specimen: 80mm;
- Width of the specimen: 10mm;
- Standard followed: ISO 14125.

Before undergoing the mechanical tests, the specimens are conditioned for 2 days in a room regulated at 23°C and 48% humidity..

3.2.5 *Rheological trials*

The material is first steamed for 24 hours at 55°C. The capillary rheometer used is a Göttfert RG 20. In order to study the rheological behavior during the injection, the temperature applied corresponds to that of the injection, i.e. 190°C. The rheology cycle defined in table 2 makes it possible to start the rheology cycle at high shear rates, modeling the injection process.

Tableau 2 : paramètres des essais rhéologiques

Température (°C)	Taux de cisaillement (s^{-1})	Filière L/d (mm)	Tolérance (%)
TS1 : 190 - TS2 : 190 - TS3 : 190	1000 - 2000 - 5000 - 10000	30/1 - 20/1 - 10/1	5

3.2.6 *SEM Observation*

The samples are observed using a Joel JSM-IT 500HR scanning microscope. They underwent a nitrogen fracture beforehand and then sputtering thin layers of gold in an Edwards cathode sputtering device.

3.3 *Results and discussion*

The summary of the tests carried out is presented in the table 3.

Tableau 3 : essais réalisés

Cycle	Origine du broyat avant injection	Type d'éprouvette après injection
Cycle 0	Broyat des plaques thermocompressées	Éprouvette avec 1 cycle d'injection
Cycle 1	Granulés obtenus par le broyage des éprouvettes ayant subies 1 cycle d'injection	Éprouvette avec 2 cycles d'injection
Cycle 2	Granulés des éprouvettes ayant subies 2 cycles d'injection	Éprouvette avec 3 cycles d'injection
Cycle 3	Granulés des éprouvettes ayant subies 3 cycles d'injection	Éprouvette avec 4 cycles d'injection

Note that for the first injection cycle (cycle 0), the material is the shredded material of the thermocompressed plates. As the shredded material has a very low density, the passage from the hopper to the screw is difficult, it is necessary to stir the material so that it is carried away by the injection screw. In addition, the last cycle (cycle 3) could not be fully completed because the material became too fluid to be injected. Figure 5 clearly shows that the material came out of the mold cavity.

Figure 5 : éprouvettes du cycle 3

3.3.1 *Influence of the number of cycles*

Table 4 presents the mechanical results of the specimens according to the injection cycles. Due to manufacturing problems in cycle 3, the material is characterized only in tension because few specimens were obtained.

Tableau 4 : résultats mécaniques des essais de traction et de flexion

Essais	Cycle	Module (MPa)		Contrainte à la rupture (MPa)		Déformation à la rupture (%)	
		Valeur	Écart-type	Valeur	Écart-type	Valeur	Écart-type
Traction	Cycle 0	6857,8	215	43,94	0,7	1,44	0,14
	Cycle 1	6471,9	327	39,97	0,5	1,08	0,06
	Cycle 2	6075,4	193	32,07	0,7	0,69	0,03
	Cycle 3	6115,6	246	20,23	5,0	0,38	0,09
Flexion	Cycle 0	6234,9	116	92,20	0,7	2,12	0,05
	Cycle 1	5521,4	143	73,70	0,9	1,60	0,04
	Cycle 2	5498,0	139	52,70	1,9	1,04	0,04

The results obtained agree with the values presented in the literature ([3], [7], [8], [9]). Thus, the Young's modulus and the breaking stress decrease as a function of the cycles. In tension, the modulus decreases little over 4 injection cycles (-11%) unlike the breaking stress which drops by 46% between the first and the last cycle. Similarly for the bending tests, the modulus and the stress decrease according to the number of cycles carried out. The modulus drops by 12% while the stress decreases by 38% after cycle 2.

Table 4 and figure 6 show an increasingly fragile behavior of matter. This phenomenon is confirmed via the SEM images (figure 7). They highlight an increasingly brittle fracture surface depending on the injection cycle.

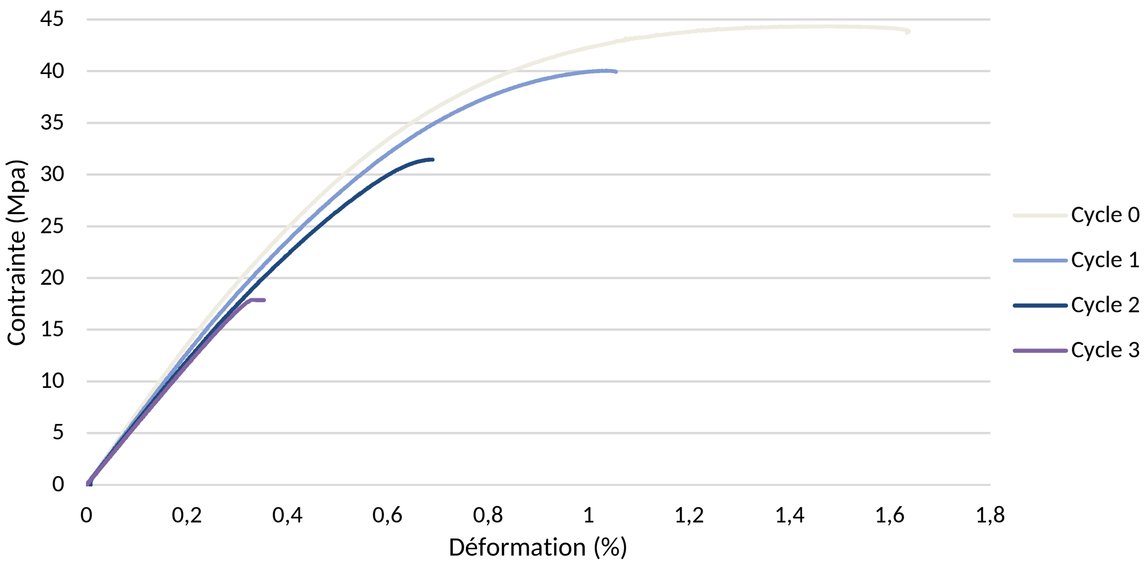
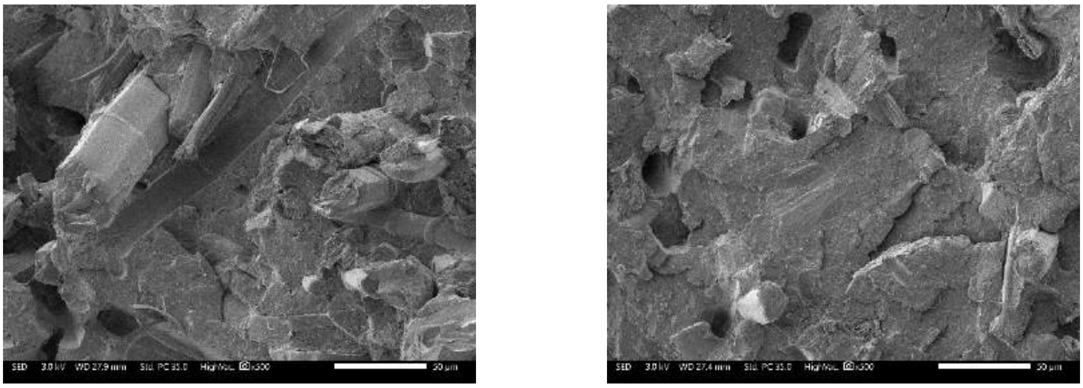


Figure 6: comportement de la contrainte en fonction de la déformation pour chaque cycle d'injection en traction



a) Cycle 0 b) Cycle 2

Figure 7: faciès de rupture de traction du cycle 0 (a) et cycle 2 (b)

These tensile and bending tests give encouraging mechanical results for recycling Kairlin® by injection. However, this recycling process cannot be repeated too many times due to the drop in mechanical properties over the injection cycles, revealing a significant degradation of the material. Optimization of the process, in particular by adding an extrusion step, can improve the properties and thus allow better recyclability of Kairlin®. However, Le Duigou [8] indicates that the grinding methods before injection have a strong impact on the distribution of fiber lengths and therefore the mechanical properties. This process will inevitably lead to a reduction in the mechanical properties which can be counterbalanced by adding virgin material.

3.3.2 *Rhéological trials*

Initially, shear rates are imposed: 10, 50, 100, 500, 1000, 2000, 5000, 10000 s-1 for dies of 30/1, 20/1, 10/1 with a tolerance of 5 %. The pure PLA rheology cycle was run with these parameters. However, for cycle 0 ground material, the capillary rheometer has difficulty obtaining viscosity values for low shear rates, i.e. 10, 50, 100 s-1, forcing it to consume all the material. Thinking that the problem came from the length of the fibers compared to the diameter of the die (1mm), a test with a die of 30/2 was carried out but the problem persisted. To overcome this problem, the rheology cycle was started at higher shear rates representing the shear during injection. The final settings applied are shown in the table 4.

In this study, neither the fiber content nor the test parameters vary, only the influence of the number of injection cycles on the flow properties is observable. That is, only elements such as fiber length, PLA degradation, material stiffness and strength, and fiber matrix interface will impact flow properties [10].

The graph in figure 8 shows the apparent viscosity according to the apparent shear rate for virgin PLA and cycles 1, 2 and 3. Due to the parameters used and the lack of cycle 0 material, it is not possible to compare the viscosity of virgin PLA with cycle 0. The material from cycle 1 (which has undergone two injection cycles) and virgin PLA have a very close viscosity. However, figure 8 shows a drop in the viscosity of the material from cycle 2. Consequently, the grinding and the transformation of the material via the injection process strongly degrades the material which is explained in particular by the degradation of the PLA. On the other hand, the decrease in viscosity generates an improvement of the fiber/matrix interface which is visible in the figure 8.

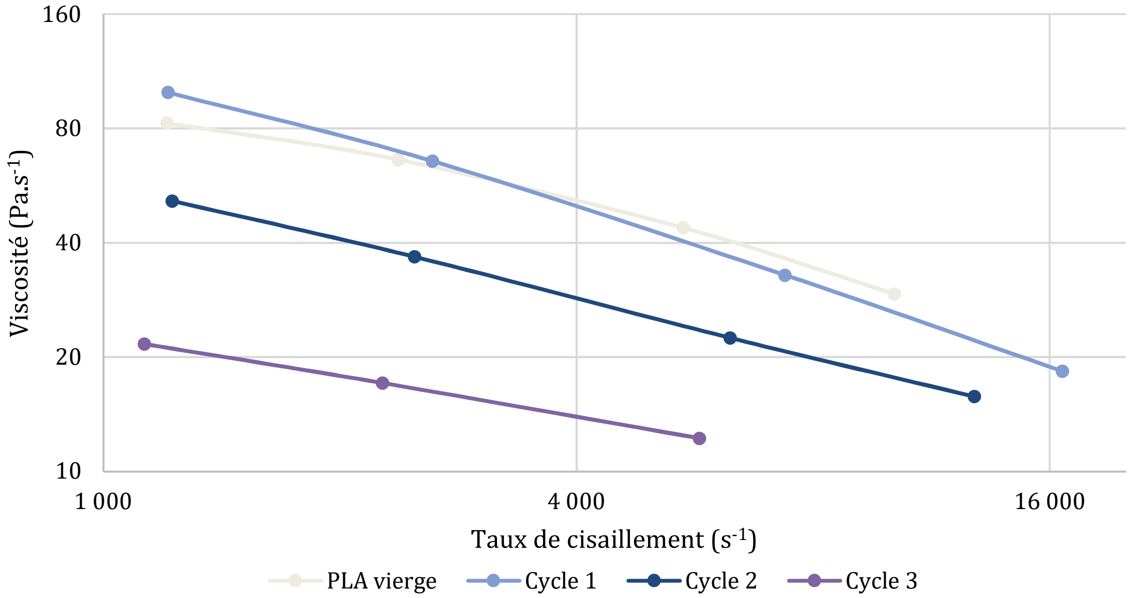
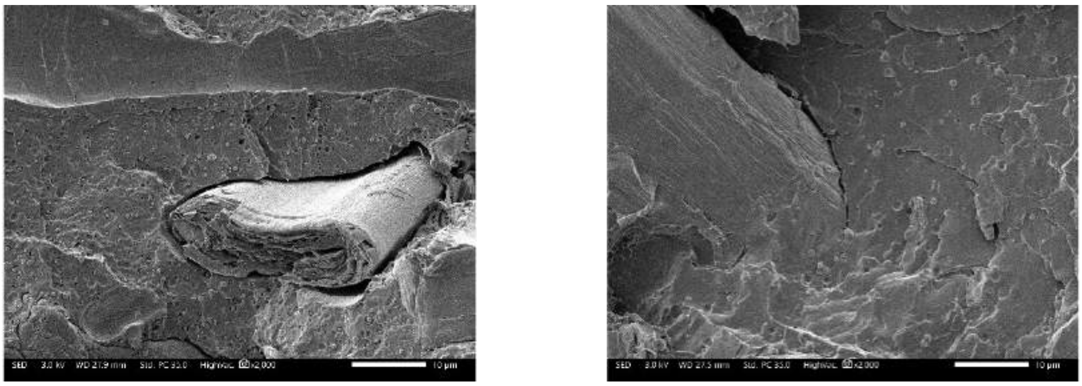


Figure 8 : viscosité en fonction du taux de cisaillement pour le PLA vierge et les différents cycles d'injection



a) Cycle 0 b) Cycle 2

Figure 9: image MEB d'une fracture azote du cycle 0 (a) et du cycle 2 (b)

Figure 9 shows good dispersion and homogenization of flax fibers in the PLA matrix. It also shows a decrease in the length of the fibers according to the number of injection and grinding cycles undergone by the material.

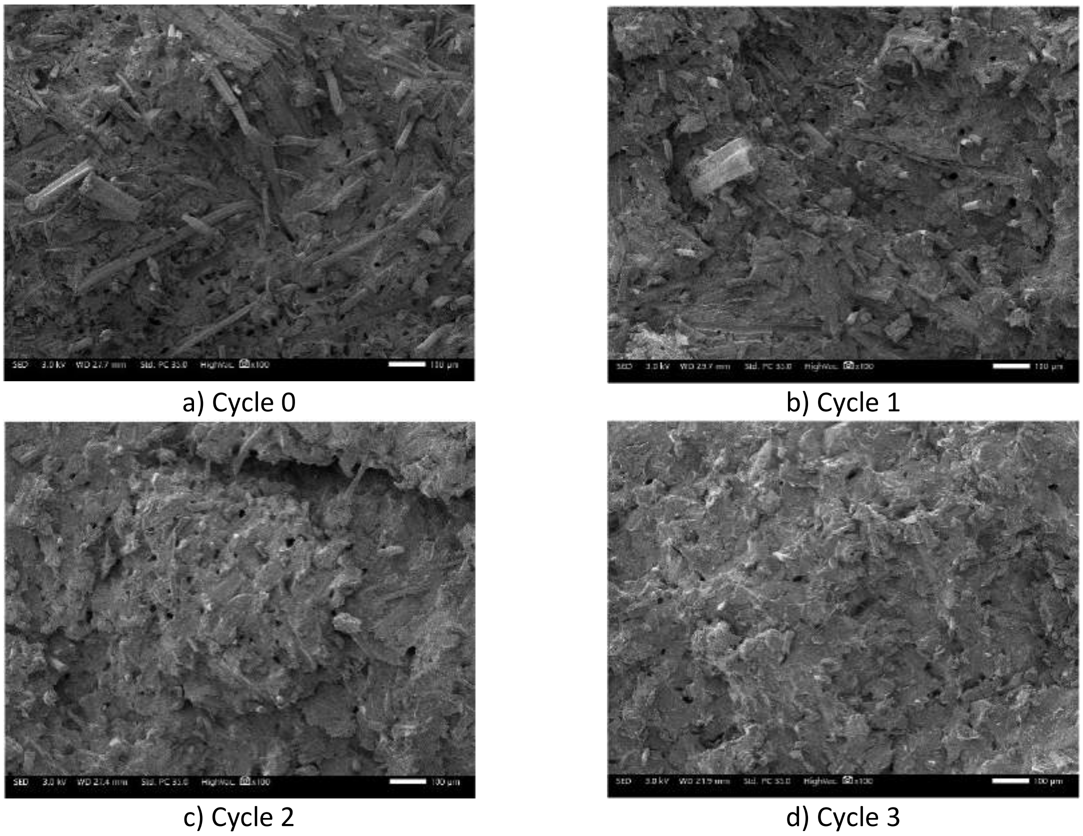


Figure 10: image MEB des faciès de rupture des essais de traction pour le cycle 0 (a), cycle 1 (b), cycle 2 (c), cycle 3 (d)

3.4 *Conclusion*

These tests made it possible to characterize the recyclability of Kairlin® since no virgin material was added. Thus, the influence of successive recycling cycles (grinding and injection) on the mechanical and rheological properties could be determined. Regarding the mechanical properties, in tension, the modulus decreases little over 4 injection cycles (-11%) unlike the breaking stress which drops by 46% between the first and the last cycle (Cycle 3). Similarly for the bending tests, the modulus and the stress decrease with the number of cycles carried out. The modulus drops by 12% while the stress decreases by 38% between the first and the penultimate cycle (Cycle 2). The specimens are more and more brittle over the cycles. Cycle 1 material (which has undergone two injection cycles) and virgin PLA have a very similar viscosity. However, a drop in the viscosity of the material appears from cycle 2. Consequently, the grinding and transformation of the material via the injection process strongly degrades the material. These reductions in both mechanical and rheological properties can be explained in particular by the reduction in the length of the fibers and the degradation of the PLA.

This method is also not viable in an industrial process since the shredded material (cycle 0 material) passes very difficultly from the hopper to the auger because of its low compactness. It is therefore necessary to stir the material so that it is carried away by the injection screw, which greatly limits the speed of the machine.

This process cannot be repeated too many times due to significant degradation of the material. However, the results obtained are very encouraging and make it possible to consider recycling Kairlin® by injection. Indeed, the addition of an extrusion step before injection and the addition of virgin material to each cycle could greatly improve the properties and optimize the process.

4 Phase 2 : injection after extrusion

The injection process is preceded by an extrusion step to improve the recyclability of Kairlin®. In addition, virgin material is added during extrusion in order to obtain mechanical properties similar to marketed injection granules.

4.1 *Materials*

Two monolithic Kairlin® are used to make up the ground material. The first is composed of:
- - 2 layers of PLA film;
- - 24 layers of Flower linen/PLA nonwoven.

The second is composed of:
- - 3 layers of PLA film;
- - 2 layers of non-woven linen/PLA.

4.1.1 Non-woven Flower flax/PLA

The preform is identical to that presented in 4.1.1.

4.1.2 Non-woven flax/PLA

The nonwoven also consists of flax reinforcement combined with polylactic acid (PLA) thermoplastic fibers by a needling process. Nevertheless, in this nonwoven, the fibers have no preferential orientation. The proportion of flax in the preform is 40% while the PLA constitutes 59.88%, the remaining 0.12% corresponds to the dye; titanium dioxide. The grammage of the nonwoven is equal to 1300g/m2.

4.1.3 PLA film

The PLA film is identical to that detailed in 4.1.2.

4.1.4 PLA pellets

PLA and PBS granules are the virgin material added during the extrusion process. PLA granules come from NatureWorks under grade 7001D. They benefit from an industrial compost certification and are bio-sourced. The Young's modulus and the maximum stress of this PLA are equal to 1670 MPa and 65 MPa respectively. PLA has an MFR of 6g/10min at 210°C and 2.16kg.

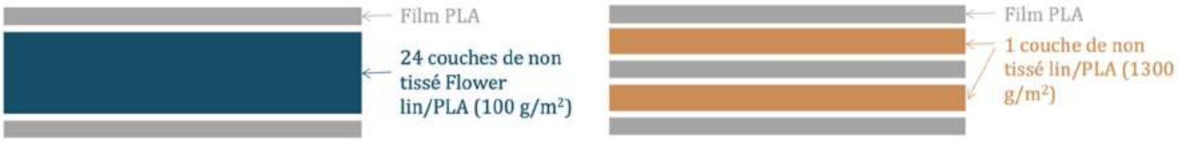
4.1.5 PBS pellets

PBS granules come from ptt MCC. They have home compost certification and are made from bio-sourced materials. The flexural modulus and the maximum stress of this PBS are equal to 630 MPa and 40 MPa respectively. PBS has a density of 1260kg/m3 an MFR of 5g/10min at 190°C and 2.16kg.

4.2 Method

4.2.1 Plate production

The assembly of the components of the monolithic plate is carried out by stacking the flax/PLA nonwovens and the PLA films following a stacking sequence. The two stacking sequences are described in figure 11.



a) drapage des plaques Flower *b) drapage des plaques*

Figure 11 : drapage des plaques Flower (a) et des autres plaques (b)

The Flower plate is made using the laboratory process described in 3.2.1, while the other plate is made using the industrial process detailed below:

- Hot pressing: pressures of 0.5 then 0.7 and finally 1 bar are applied to the draped assembly as well as two sheets serving as a mold for 8 minutes, the temperature of the plates is 210°C;
- Cooling: the assembly is moved on the plates of the cold press. Cooling takes place for 10 minutes where the temperature changes from 20°C to 28°C.

4.2.2 Composition of the ground material

Once manufactured, the plates are crushed using a CMB knife crusher with a 5mm grid. Thus, two ground materials of different composition are obtained. The Flower plate shredded material contains 29.4% flax fibres, 70.2% PLA and 0.4% carbon black. The other ground material is composed of 26.6% flax fibres, 73.3% PLA and 0.1% titanium dioxide.

4.2.3 Extrusion process

From the two ground products produced, several formulations are made in order to load the granules more or less with flax fibres. Two reference products are also extruded, these are PLA 7001D and a mixture of PLA/PBS granules with 60% PLA. The five types of extruded granules are shown in Table 5. The percentages are mass percentages.

Tableau 5 : composition des différents types de granules extrudés

Type de granules	Teneur en granules de PLA vierge (%)	Teneur en PLA venant du broyat (%)	Teneur en granules de PBS vierge (%)	Teneur en fibres de lin venant du broyat (%)
PLA	100			
PLA/PBS	60		40	
(PLA/PBS) / Lin 14% Flower	19	33	34	14
(PLA/PBS) / Lin 18% Flower	7	42	33	18
(PLA/PBS) / Lin 14%	2	44	40	14

The extrusion parameters chosen are as follows:
- Screw rotation: 100 rpm;
- Machine screw: twin screw;
- Throughput: 1 kg/h
- Temperature in all areas: 180°C.

Figure 12 shows the material extrusion step. After this step, the filaments are cut into granules. Thus, figure 13 shows the difference between the shredded material to be recycled and the granules ready to be injected.

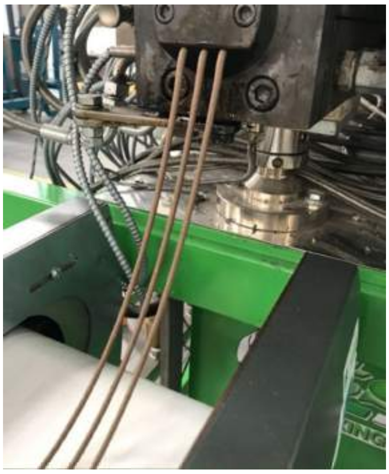


Figure 12 : procédé d'extrusion

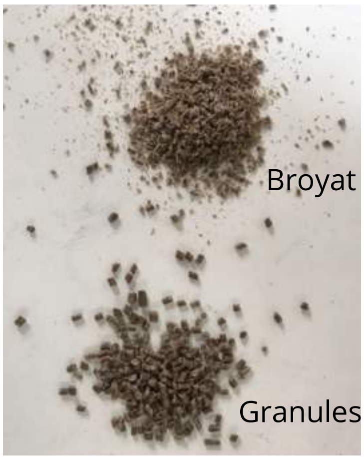


Figure 13 : différence entre le broyat et les granules extrudés

4.2.4 Injection process

The injection parameters are similar for the different formulations and presented in Table 6. For each type of granule, a dozen specimens are injected to perform the mechanical tests. The injection press used is a Battenfeld HM 80/200.

Tableau 6 : paramètres d'injection pour les essais de la phase 2

Température du moule (°C)	Pression d'injection (bar)	Temps d'injection (s)	Température d'injection (°C)	Temps de refroidissement (s)
25	1500 - 1200 -1000 - 600 - 0	9,6	180 +/- 5	20

Le cycle d'injection est décrit en figure 14. Le cycle dure au total 29,6 secondes.

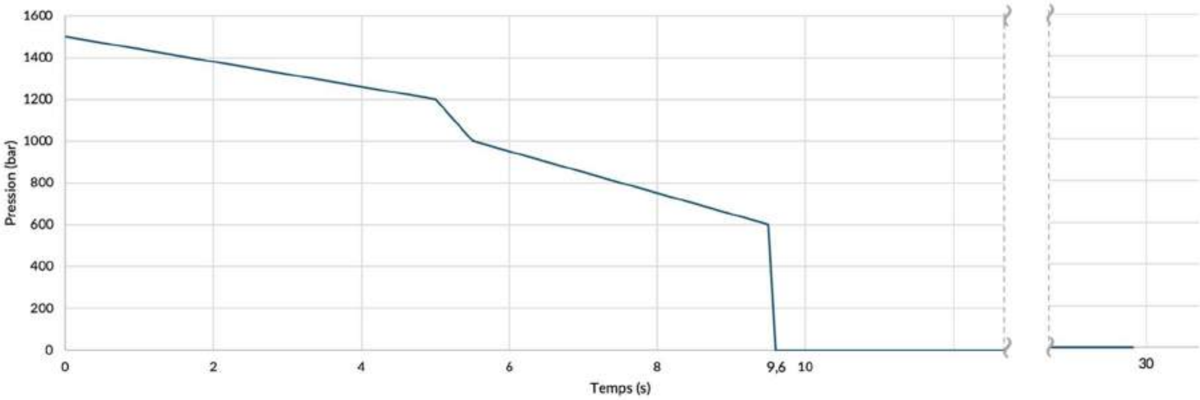


Figure 14 : cycle d'injection

4.2.5 *Mechanical trials*

Tensile and bending tests are carried out with an MTS criterion 42 equipped with a 5kN and 500N cell and an extensometer with a displacement length of 25mm. Regarding the tensile tests, the speed of movement of 1mm/min. The standard followed during the tensile tests is the ISO 527-2 standard.
The parameters chosen for the bending tests are:
- Movement speed of 2mm/min;
- Range: 64mm;
- Length of the specimen: 80mm and width of the specimen: 10mm;
- Standard followed: ISO 14125.

Before undergoing the mechanical tests, the specimens are conditioned for 2 days in a room regulated at 23°C and 48% humidity.

4.2.6 *Rheological trials*

The material is first steamed for 24 hours at 55°C. The capillary rheometer used is a Göttfert RG 20. The rheology cycle defined in table 7 makes it possible to start the rheology cycle at high shear rates, modeling the shear during extrusion and injection.

Tableau 7 : paramètres des essais rhéologiques

Température (°C)	Taux de cisaillement (s^{-1})	Filière L/d (mm)	Tolérance (%)
TS1 : 190 - TS2 : 190 - TS3 : 190	1000 - 2000 - 5000 - 10000	30/1 - 20/1 - 10/1	5

4.3 Results and discussion

The specimens obtained are all flawless. A total of 12 test specimens are obtained per type of granules. The test specimens made with the granules named "Flower" are black while those made with the granules (PLA/PBS) / Flax 14% are brown (figure 15).

Figure 15 : éprouvette injectée à partir de granules (PLA/PBS) / Lin 14%

4.3.1 Mechanical trials

Figure 15 presents the results obtained after the tensile tests. The histograms on the right for each type of formulation and in dark color correspond to the maximum tensile stress while those on the left correspond to the tensile modulus.

The addition of PBS up to 40% by mass leads to a 36% drop in modulus compared to PLA alone. The tensile moduli of the recycled formulations are situated between the two virgin materials (PLA 7001D and PLA/PBS mixture). Thus, the addition of flax fibers increases the modulus. Indeed, the formulation with 18% flax fibers has a modulus 15% higher than the formulation with 14% flax fibers and 43% compared to the virgin PLA/PBS mixture.

As for the tensile modulus, the addition of PBS leads to a 32% decrease in the maximum stress compared to PLA alone. All recycled formulations have a stress similar to the virgin PLA/PBS mixture. It therefore seems that flax fibers make it possible to compensate for the poor properties of recycled PLA. Consequently, the recycled specimens have similar tensile properties (even better in particular for the modulus) compared to the PLA/PBS reference mixture, but these are inferior to virgin PLA

7001D.

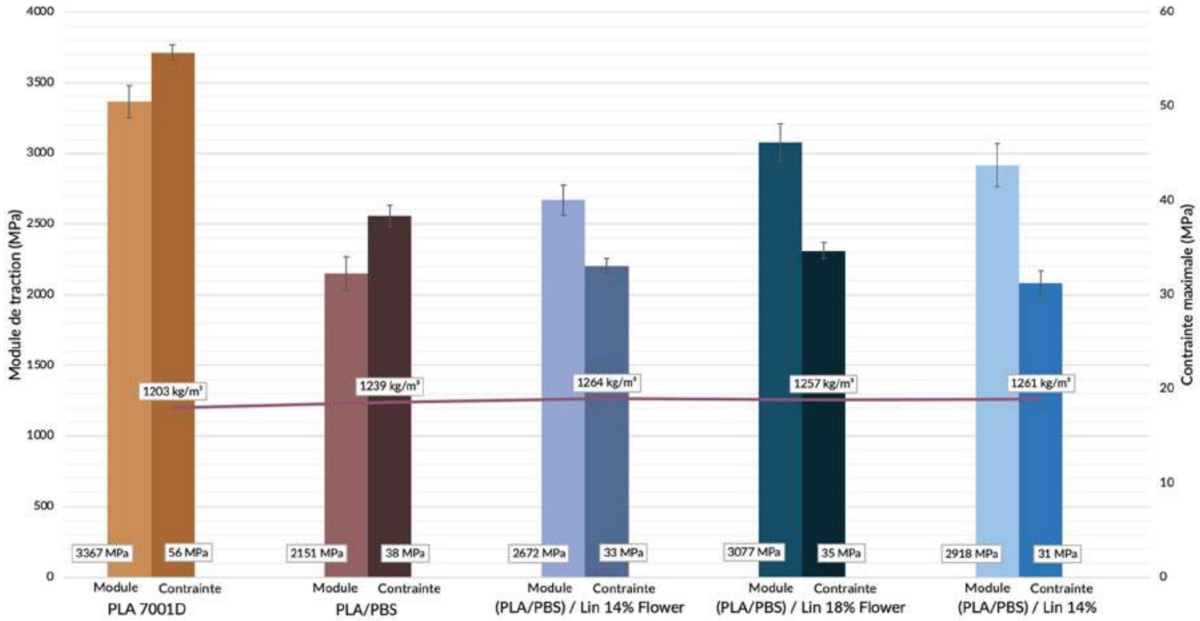


Figure 16 : module et contrainte en traction pour les différentes formulations

Figure 17 presents the results obtained after the bending tests. The histograms on the right and in dark color correspond to the maximum stress in bending while those on the left correspond to the modulus of bending.

The behavior of the bending modulus is similar to that in tension. The addition of PBS leads to a 35% decrease in modulus compared to PLA alone. The flex moduli of recycled formulations lie between the two virgin materials. Thus, the addition of flax fibers increases the modulus. Indeed, the formulation with 18% flax fibers has a modulus close to virgin PLA and 18% higher than the formulation with 14% flax fibers and 45% compared to the virgin PLA/PBS mixture.

The addition of PBS also results in a 35% decrease in maximum stress compared to PLA alone. Recycled PLA is more present in the (PLA/PBS)/Linen 14% formulation than in the same Flower formulation, 44% versus 33% respectively (see Table 8). However, the stress is lower for the first formulation meaning that the recycled PLA degrades the maximum stress. All recycled formulations have lower stress than the virgin PLA/PBS blend. It therefore seems that flax fibers do not make it possible to counterbalance the weak properties of recycled PLA. However, the higher the flax fiber content, the greater the maximum stress. For example, the formulation with 18% flax fibers has an 8% higher modulus compared to a formulation comprising 14% flax fibers.
Therefore, the recycled specimens have very good flexural moduli but have a slightly lower maximum stress compared to the PLA/PBS reference mixture.

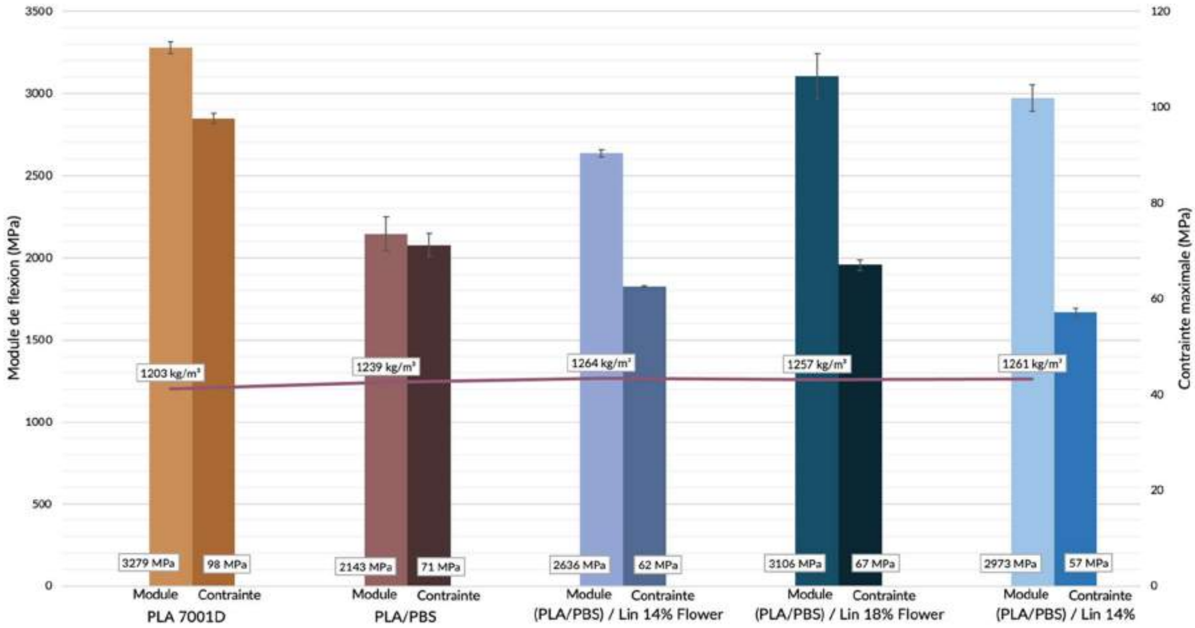


Figure 17 : module et contrainte en flexion pour les différentes formulations

4.3.2 Rheological trials

The graph in FIG. 18 shows the apparent viscosity as a function of the apparent shear rate for PLA alone, PLA/PBS and the other types of granules containing flax fibers. The viscosities of the different formulations remain globally close to the reference material; the PLA/PBS mixture. The formulation (PLA/PBS) / Flax 14% has the same PLA fibers as the black PLA fibers, the only difference comes from the dye. However, the dye, due to its low presence (less than 1% by mass), does not influence the behavior of these two fibers, they are therefore identical. Thus, the difference in viscosity evolution between (PLA/PBS) / Lin 14% Flower and (PLA/PBS) / Lin 14% comes from its formulation. The first is loaded more with virgin PLA (19%) while the second contains almost only recycled PLA (2% virgin PLA). Recycled PLA therefore degrades the rheological behavior of formulations, especially for low shear rates.

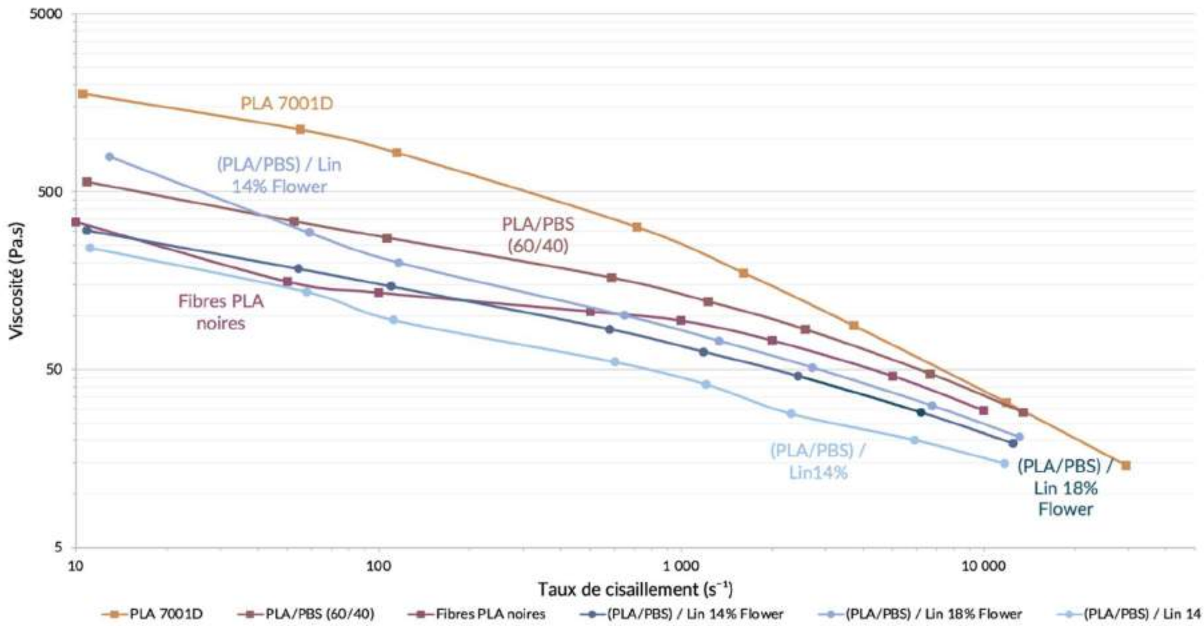


Figure 18 : viscosité en fonction du taux de cisaillement pour différentes formulations

Similarly, the comparison between the formulations (PLA/PBS) / Lin 14% Flower and (PLA/PBS) / Lin 18% Flower shows that the higher the rate of recycled PLA, the lower the viscosity depending on the shear rate. . Indeed, these two formulations have the same rate of PBS but a higher recycled PLA rate of 10% for the formulation (PLA/PBS) / Flax 18%. The influence of flax fibers is very weak for high shear rates. Indeed, black PLA fibers are not suitable for extrusion unlike PLA 7001D. Figure 18 shows that the viscosity is lower for black PLA fibers as a function of shear rate compared to PLA 7001D. This observation is all the more heightened for low shear rates. Thus, at this level, the black PLA fibers are more responsible for the drop in viscosity, concurring with the observations made previously. This is due to the manufacturing process of PLA fibers. Indeed, during the spinning process thereof, high shear rates are applied degrading the material. The molar mass is therefore greatly reduced. PLA fibers are therefore not suitable for the extrusion process because they have already been degraded upstream.

The extrusion and injection processes stress the material with high shear rates, between 5000 and 10000 s-1. It is therefore necessary to favor low rates of recycled PLA in order to get as close as possible to the behavior of virgin materials.

4.3.3 Impact resistance trials

Charpy impact resistance tests of unnotched specimens are carried out according to the ISO 179 standard. Indeed, this is a property required for the injection field. According to figure 18, the addition of recycled material (linen and black fibers of PLA) reduces the impact resistance by half. Thus, the energy required to deform and break the recycled specimens during an impact is reduced. In fact, flax fibers do not have good shock resistance. Similarly, PLA has low impact resistance, around 10 kJ/m²). Normally, the value of (PLA/PBS) / Flax 18% Flower should be more than that of (PLA/PBS) / Flax 14% because the former formulation contains more flax fibers and less PBS. In order to improve the impact resistance, it is necessary to increase the rate of PBS and/or add plasticizer.

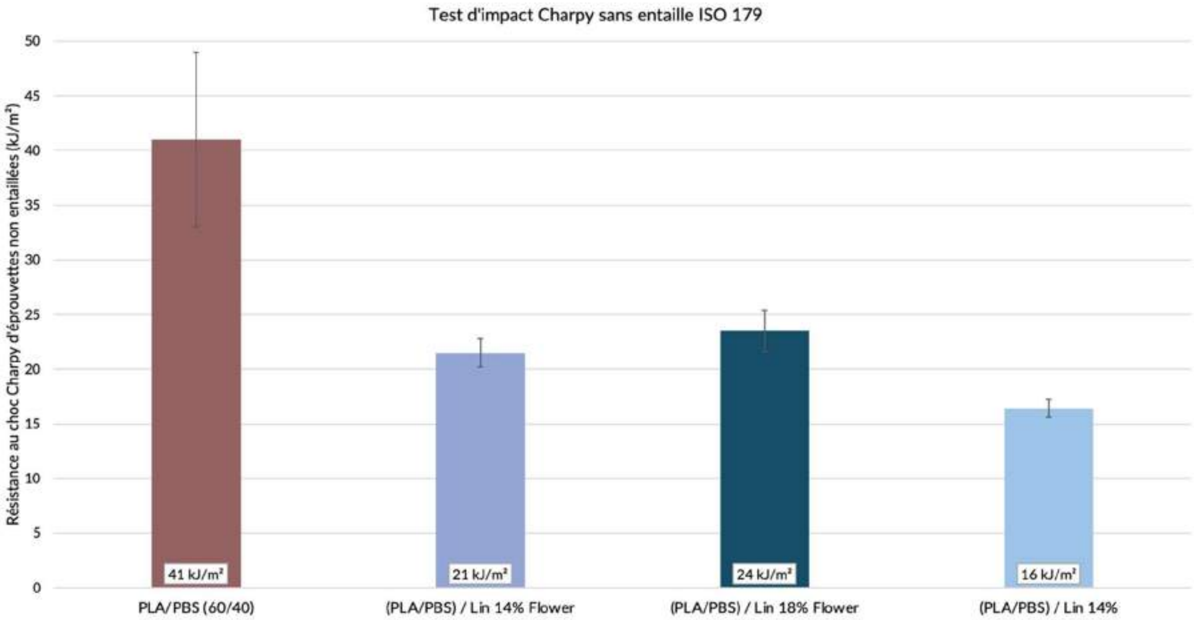


Figure 19 : résultats des tests de résistance au choc pour les différents types d'éprouvettes

4.3.4 Comparison to other injection products

The mechanical and rheological results obtained are compared with the technical data sheets of marketed products in order to know if this upgrading method is viable. Table 8 presents the technical data of a product used in the field of injection, called LinoTech. Table 9 presents the technical characteristics of a customer specification.

Tableau 8 : données techniques d'un produit commercialisé appelé LinoTech

Propriété		Norme	Conditions	Valeur	Unités
Physique	Masse volumique	ISO 1183		1,24	g/m^3
Traction	Contrainte en traction	ISO 527		40	MPa
	Module de traction			3658	MPa
	Déformation à la rupture			1,9	%
Résistance au choc	Test d'impact Charpy sans entaille	ISO 179-1	23°C	10	kJ/m^2
Rhéologie	Melt Flow Rate	ISO 1133	190°C – 2,16kg	13	g/10min

Tableau 9 : caractéristiques techniques du cahier des charges client

Propriété		Norme	Conditions	Valeur	Unités
Flexion	Module de flexion	ASTM-D-790		2070	MPa
Résistance au choc	Test d'impact Charpy sans entaille	ASTM-D-258	23°C	83	J/m
Rhéologie	Melt Flow Rate	ASTM-D-1238	190°C – 2,16kg	4	g/10min

The mechanical properties are displayed in figure 20. The tensile moduli and stresses are slightly lower than those of the reference product. However, by improving the formulations, for example by changing the percentage of PBS, the properties of the recycled formulations could approach the reference product. Regarding the deformation at break, two of the recycled materials exceed the reference material. The last formulation (PLA/PBS) / Flax 14% has a deformation at break similar to that of the reference.

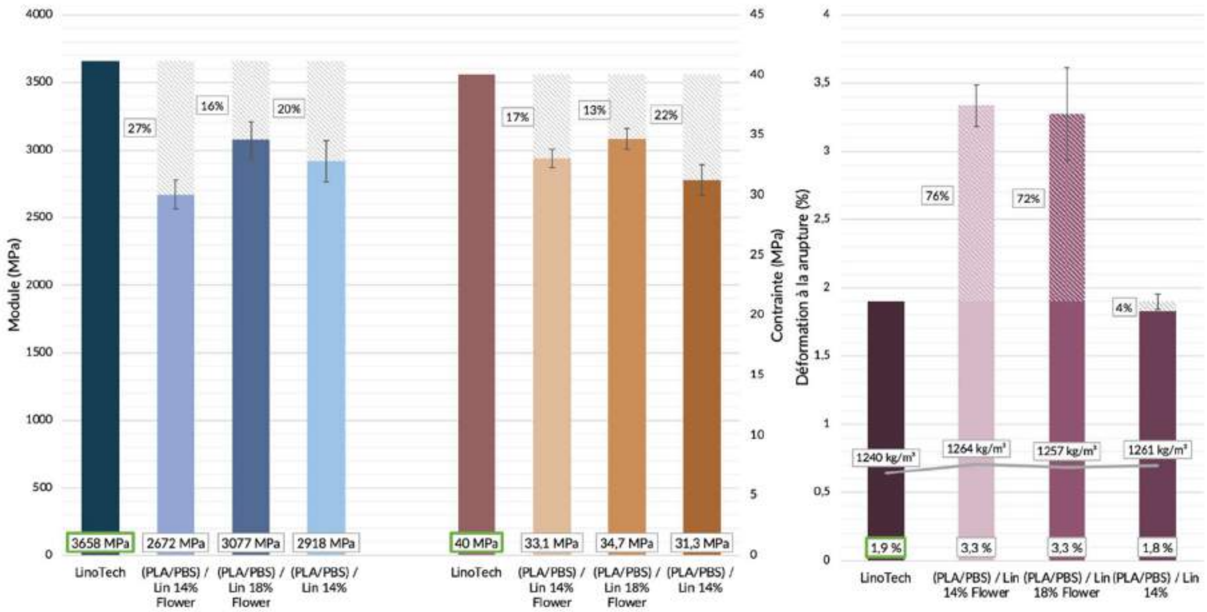


Figure 20 : comparaison des propriétés en traction des éprouvettes avec celle du produit LinoTech

The results of the impact resistance tests and MFI tests are shown in Table 10. Recycled materials have twice the impact resistance of the LinoTech reference.

Tableau 10 : résultats d'impact Charpy sans entaille ISO 179 et de tests MFI

	LinoTech	(PLA/PBS) / Lin 14% Flower	(PLA/PBS) / Lin 18% Flower	(PLA/PBS) / Lin 14%
Résistance au choc Charpy d'éprouvettes non entaillées (kJ/m^2)	10	21	24	16

MFI (g/10min)	13	12	22	13

The diagram in figure 21 makes it possible to position the recycled products in relation to the competitor's product and the customer's specifications. According to the results, although the mechanical properties are not all similar to that of the LinoTech product, the three formulations show properties at the height of the marketed products. These results are all the more encouraging as the formulations are not optimized, they can thus be optimized according to each industrial application..

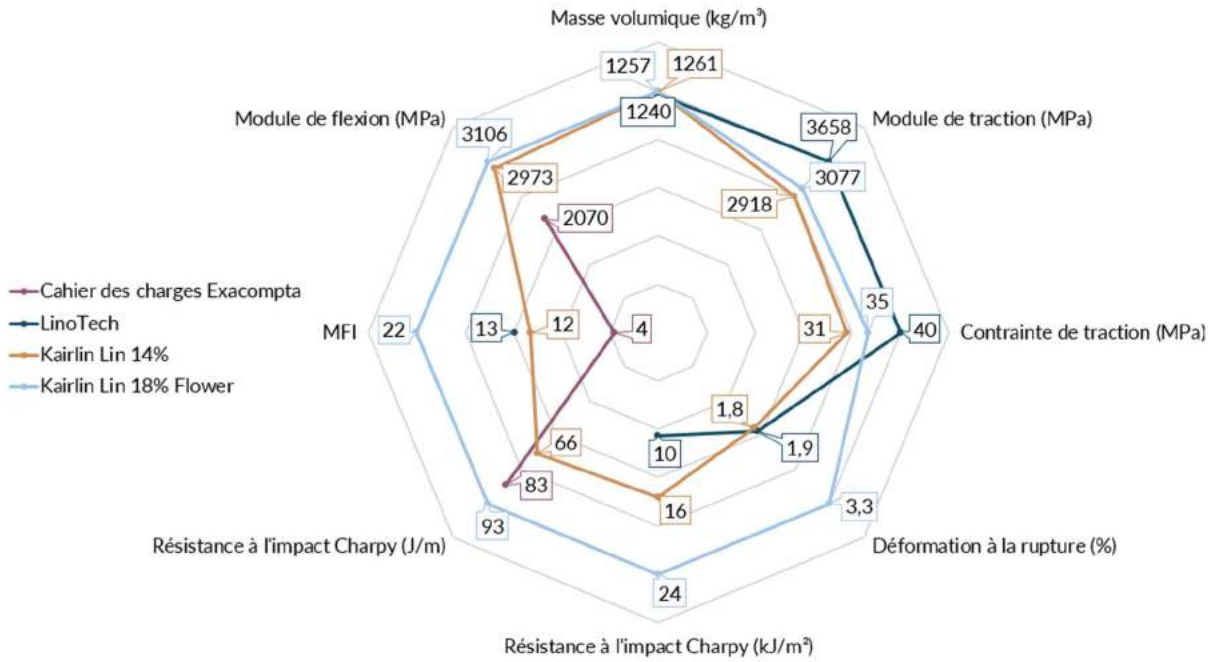


Figure 21 : propriétés de deux produits recyclés comparés au produit concurrent et au cahier des charges client

The LinoTech material has already been tested on injected products. However, this material was very brittle. Indeed, after a fall the product had broken in two. Thus, to get closer to the customer's specifications, it will be necessary to add PBS in order to obtain a higher impact resistance. It is noted that talc makes the material more rigid and therefore more brittle. However, the LinoTech product contains it, so this also accentuated the low impact resistance of the injected product..

4.3.5 Comparison with other recycling processes

In order to determine the mechanical losses during recycling, it is necessary to compare injected recycled Kairlin® with other recycled Kairlin® and with virgin Kairlin®.

Two injected formulations are compared to the other materials. The first are obtained during cycle 1, i.e. specimens that have undergone two injection cycles without an extrusion step. Material from cycle 0 (material that has undergone a recycling cycle and comes from shredded industrial plates) is excluded during the comparison because it is difficult to pass from the hopper to the injection screw. This is a problem not acceptable for an industrialist, this material is therefore unusable. The second injected formulation used for the comparison comes from the formulation (PLA/PBS) / Flax 18% Flower.
Virgin Kairlin® sheets are manufactured using the industrial process described in 4.2.1. The draping is identical to the sheets made in 4.2.1, however the virgin Kairlin® sheets entitled "Flower" have 6 layers of nonwoven Flower of 100g/m2 and not 24. The other virgin Kairlin® sheets are identical to the one presented in b) figure 11.

Recycled Kairlin® sheets are manufactured using a laboratory process called the thousand-sheet process. This process consists in incorporating between each layer of nonwovens of the shredded material. The nonwovens are all composed of 40% fibers, 59.4% PLA and 0.6% carbon black. Their weight is 350g/m2. A quantity of 60% ground material by mass is added between each layer of nonwoven with a homogeneous distribution over the entire surface. This ground material consists of 70% PLA and 30% flax fibers.

Recycled Kairlin® sheets and virgin Kairlin® sheets, produced by the thermocompression process, are tested in both directions. To simplify the reading, the values presented in figure 21 are the highest. Thus, for virgin plates, the values in the direction of unwinding of the coil (MD) are displayed while for recycled plates the values are those of the direction opposite to the direction of unwinding of the coil (CD).

All materials compared are summarized in Table 11.

Tableau 11 : matériaux utilisés pour la comparaison

Type	Procédé	Taux de broyat	Non tissé			Grammage de la plaque (g/m^2)
			Provenance et nombre	Grammage (g/m^2)	Orientation de la fibre	
Flower	Industriel	0%	6 NT Écotechnilin	100	Légère	2070
Kairlin®	Industriel	0%	2 NT Écotechnilin*	1300	Non	3905
Cycle 1	Injection	100%	Composition de la plaque broyée : 24 NT Écotechnilin légèrement orientés (grammage des plis : $100g/m^2$)			
(PLA/PBS) / Lin 18% Flower	Extrusion puis injection	60%	Composition de la plaque broyée : 24 NT Écotechnilin légèrement orientés (grammage des plis : $100g/m^2$) Ajout de 7% de PLA vierge et 33% de PBS vierge			
NTe60 MF	Labo mille feuilles	60%	4 NT Écotechnilin	350	Non	5675

*composition identique à celle présentée en figure 11 b

The bending results of these different materials are presented in figure 22. Only the bending property is compared for all the materials.

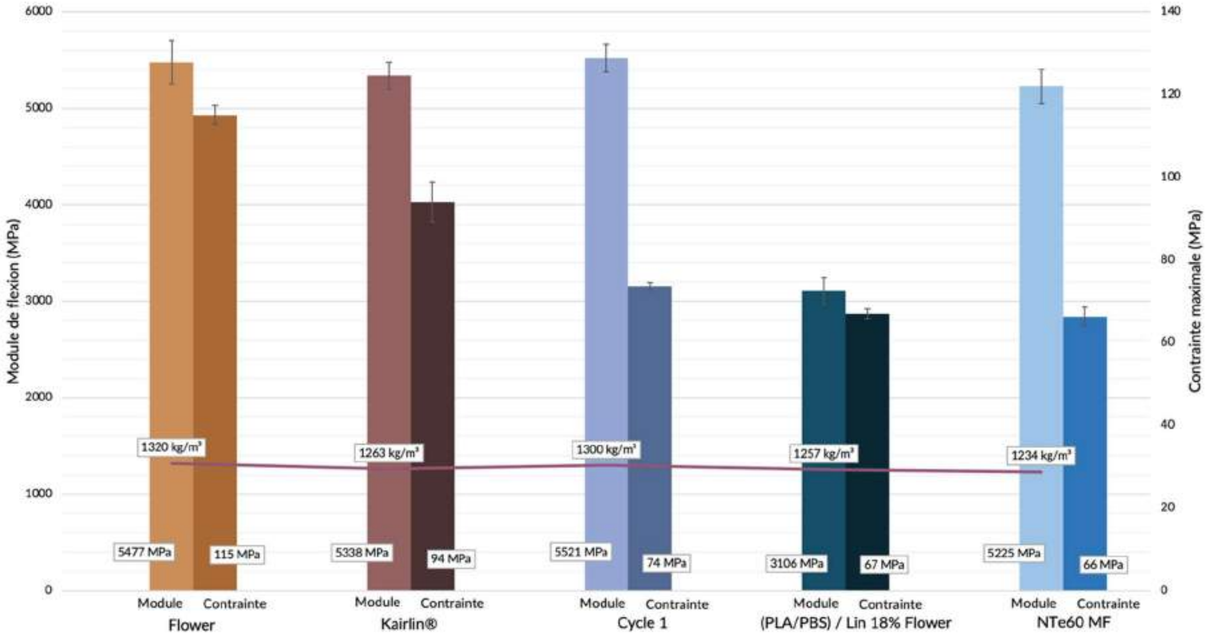


Figure 22 : comparaison des propriétés mécaniques en flexion

The results show that the mechanical properties of the specimens manufactured by injection (Cycle 1) are slightly superior to those of the plates recycled by thermocompression with nonwoven non-oriented. These two recycling routes have great potential since the bending moduli are equivalent to those of the reference plates. However, recycled materials regardless of their process have lower maximum stresses than those of the reference plates. Indeed, the degradation of PLA fibers and the reduction in fiber length due to mechanical recycling greatly alters the stress.

The value of the flexural modulus of the specimens (PLA/PBS) / Flax 18% Flower is very low compared to other recycled materials and in particular that of Cycle 1 (composed only of shredded material). The 56% drop between the modulus of Cycle 1 and that of the formulation (PLA/PBS) / Flax 18% Flower is explained in particular by the addition of raw materials, in particular PBS which has a low flexural modulus (650MPa) but also by a lower fiber content, 18% against 29% for Cycle 1. The compositions of the materials are given in table 12.

Tableau 12 : composition en pourcentage massique des différentes matières comparées

	Flower	Kairlin®	Cycle 1	(PLA/PBS) / Lin 18% Flower	NTe60 MF
Teneur en PLA (%)	76,5	73,3	70,2	7	71,5
Teneur en colorant (%)	Noir - 0,3	Blanc - 0,1	Noir - 0,4	Noir - proche 0	Noir - 0,5
Teneur en PLA 7001D (%)				42	
Teneur en PBS (%)				33	
Teneur en fibres de lin (%)	23,2	26,6	29,4	18	28

Finally, Cycle 1 has very good mechanical properties but is not technically feasible. Indeed, the cycle 0 material passes very difficultly from the hopper to the auger because of its low compactness. It is therefore necessary to stir the material so that it is carried away by the injection screw, which greatly limits the speed of the machine. This material is therefore not feasible on an industrial scale. These results are however very encouraging since the material (PLA/PBS) / Linen 18% Flower can be improved by changing the formulation and thus approach the properties of the reference plates..

4.4 Conclusion

Compared to Kairlin® recycled by thermocompression, the extruded and injected specimens have a lower modulus but a similar stress. Their properties are also weaker compared to virgin materials due to the degradation of PLA fibers and the reduction in fiber length during recycling. These results are nevertheless very encouraging because the formulations are not optimized, so they can be optimized according to each industrial application. Moreover, in comparison to marketed products, the three formulations show similar properties. It is also possible to improve these materials by modifying the formulas, for example by adding fillers. Talc, for example, increases the mechanical properties, cools the material more quickly and limits rotting and shrinkage during the injection process. Nevertheless, it can make the material more brittle, it will therefore be necessary to compensate by adding PBS. The addition of plasticizer can also improve the viscosity of the material or the behavior between the material and the machine. It will be necessary to pay attention to the number of injection cycles that the material has undergone in order to avoid too many transformations because it degrades very quickly. It will also be necessary to take care to minimize the injection cycle time since it determines the cost. However, this depends on the thickness of the product and the viscosity of the material. It is therefore necessary to control the viscosity of the material to be neither too viscous nor too fluid and correspond exactly to the customer's specifications. Indeed, if the material is too fluid, this can cause burrs or leaks. In addition, the viscosity influences the weld lines, which are also dependent on the injection points. Injection is therefore highly dependent on rheology and fluidity. Any improvement must be carried out taking into account the cost it generates.

5 Phase 3

During the last phase, another way of recycling is investigated. After the extrusion step, the material is transformed into 3D filament for 3D printing.

5.1 *Materials*

The monolithic Kairlin® used to constitute the ground material is composed of:

- - 2 layers of PLA film;
- - 24 layers of Flower linen/PLA nonwoven.

5.1.1 Non-woven Flower flax/PLA

The preform is identical to that presented in 4.1.1.

5.1.2 PLA

The PLA film is identical to that detailed in 4.1.2.

5.1.3 PLA and PBS pellets

The PLA and PBS granules are identical to those detailed in 4.1.4 and 4.1.5 respectively.

5.2 Method

5.2.1 Plate production

The assembly of the components of the monolithic plate and the manufacturing process are identical to those described in 3.2.1. These plates are then crushed using a CMB knife crusher to form particles 5mm in diameter. The shredded material of these Flower plates contains 29.4% flax fibres, 70.2% PLA and 0.4% carbon black.

5.2.2 Extrusion process

From the ground material, a formulation is made in order to produce the 3D filament. Thus, a mixture of 31% virgin PLA, 23% PLA fibers from shredded material, 36% virgin PBS and 10% flax fibers is extruded and then cut into granules. The contents of each component are expressed in mass percentage.

The extrusion parameters chosen are identical to those described in 4.2.3.

5.2.3 Injection process

The injection process is identical to that described in 4.2.4.

5.2.4 Realization of the 3D filament

For the extrusion of the filament, the temperature is equal to 180° C. in all the zones. The speed of the single-screw is equal to 20 rpm. The line speed is gradually adjusted and finally equal to 2.2 m/min. All the parameters are schematized on the interface of the machine and shown in figure 23.

Figure 23 : paramètres choisis sur l'interface de la machine

5.2.5 *Mechanical trials*

Tensile and bending tests are carried out with an MTS criterion 42 equipped with a 5kN and 500N cell and an extensometer with a displacement length of 25mm. Regarding the tensile tests, the speed of movement is 1mm/min and the standard is followed is the ISO-527-2 standard. Regarding the bending tests, the tests were carried out in accordance with the ISO 178 standard.

Before undergoing the mechanical tests, the specimens are conditioned for 2 days in a room regulated at 23°C and 48% humidity.

5.3 Results and discussion

5.3.1 Visual aspect

Throughout the extrusion of the 3D filament, it is difficult to keep a constant diameter around 3mm and not exceeding +/- 0.1mm. Thus, the X dimension and the Y dimension are not always identical, creating a non-constant diameter. The filament is therefore irregular and the defects are observable with the naked eye.

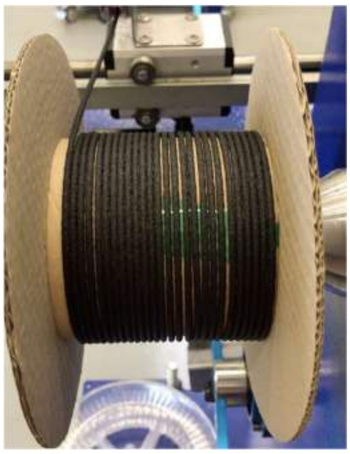


Figure 24 : enroulement du filament 3D

Despite the apparent defects of the filament, several 3D parts are printed including supports (figure 25) and specimens (figure 26) using a 2mm diameter nozzle. As the diameter is large, the appearance of the parts is coarse. To refine the surface appearance, the diameter of the nozzle should be reduced.

However, it is not possible to do this because of the presence of flax fibers. Indeed, if the diameter were reduced, the fibers could obstruct the passage.

Figure 25 : supports imprimés en 3D

Figure 26 : éprouvette réalisée en impression 3D

5.3.2 Mechanical trials

The results of the mechanical tests carried out are recorded in the table 13.

Tableau 13 : résultats mécaniques obtenus pour les éprouvettes imprimées en 3D

	Module (MPa)	Contrainte (MPa)	Déformation à la rupture (%)
Traction	1613 +/- 357	26,3 /- 0,5	2,74 +/- 0,18
Flexion	8503 +/- 230	85,7 +/- 3,1	1,70 +/- 0,20

The tensile properties are low because the specimens are very porous. On the other hand, the flexural properties are similar to virgin plates. These results are quite amazing.

5.3.3 SEM results

All the small dark gray pieces represent the PBS, the PLA is the lighter part. Thus the mixture is very homogeneous. The porosities that were observed with the naked eye are clearly visible on the first two images of figure 5 since they are indicated by the black spots. The filament is therefore homogeneous but has a major porosity defect.

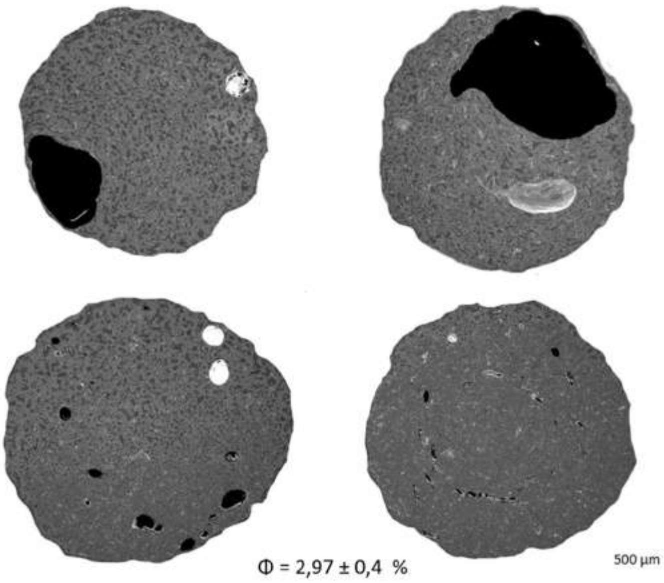


Figure 27 : section du filament 3D observée au MEB

Figure 28 shows the profile of a 3D printed part. Thus, the lower layer is well filled since it is placed on a support. On the other hand, the upper layer is very sparsely filled and shows several cavities. This is explained in particular by the large diameter of the nozzle. For comparison, the SEM profile of a plate made with the nonwovens and used to make up the shredded material is presented in figure 29.

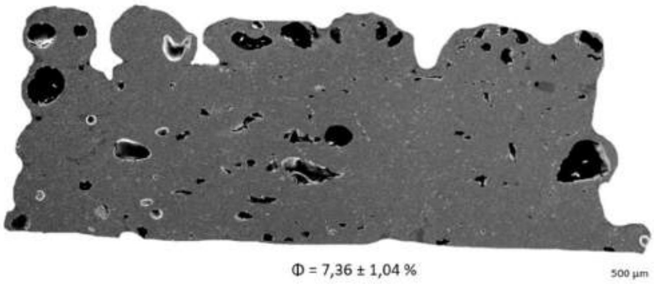


Figure 28 : profil d'une pièce imprimée en 3D

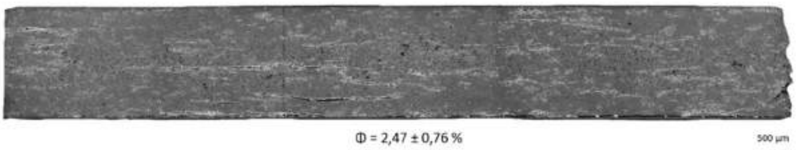


Figure 29 : image MEB d'une plaque Flower réalisée avec le procédé industriel

5.4 Conclusion

Printed objects have an imperfect surface appearance. In order to achieve better quality printed parts, the size of the nozzle should be reduced. However, reducing the size of the nozzle presents a risk of clogging it due to the presence of fibers. On the other hand, this recycling solution creates a porous filament and a non-constant diameter. Thus, if this path is considered, it will be necessary to improve the material and the process in order to obtain a better filament.

Conclusion

The first step of this study consisted of injection without going through an extrusion step. However, it turns out that this method is not viable in an industrial process since the shredded material (material from cycle 0) passes with great difficulty from the hopper to the auger because of its low compactness. It is therefore necessary to stir the material so that it is carried away by the injection screw, which greatly limits the speed of the machine. In addition, the successive grinding and transformation of the material via the injection process strongly degrades the material. These reductions in both mechanical and rheological properties can be explained in particular by the reduction in the length of the fibers and the degradation of the PLA. Therefore, this process cannot be repeated too many times due to significant degradation of the material.

Extrusion and then injection tests were then carried out. The results of these tests are very encouraging because the formulations produced in the laboratory have properties similar to those of marketed products. In addition, the formulations are not optimized, so they can be optimized according to each industrial application. It is also possible to improve these materials by modifying the formulas, for example by adding fillers. It will be necessary to pay attention to the number of injection cycles that the material has undergone in order to avoid too many transformations because it degrades very quickly. It will also be necessary to take care to minimize the injection cycle time since it determines the cost. However, this depends on the thickness of the product and the viscosity of the material. It is therefore necessary to control the viscosity of the material to be neither too viscous nor too fluid and correspond exactly to the customer's specifications.

The last way of recycling was to create filaments for 3D printing. Printed objects have an imperfect surface appearance. In order to achieve better quality printed parts, the size of the nozzle should be reduced. However, reducing the size of the nozzle presents a risk of clogging it due to the presence of fibers. On the other hand, this recycling solution creates a porous filament and a non-constant diameter. Thus, if this path is considered, it will be necessary to improve the material and the process in order to obtain a better filament.

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