Effect of recycling on mechanical behaviour of biocompostable flax/poly(l-lactide) composites

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Abstract:

The biocompostability of natural fibre-reinforced biopolymers, also known as biocomposites, makes them attractive alternative to glass fibre-reinforced petrochemical polymers. The aim of this work is to study the capacity of flax/PLLA (poly(l-lactide)) biocomposite (20% and 30% fibres by weight) to be recycled. Mechanical properties were evaluated initially, and shown to be similar to those of glass/PP and superior to hemp/PP and sisal/PP composites. Then after repeated injection cycles tensile properties were shown to be conserved until the third cycle. Matrix degradation and fibre aspect ratio were followed using molecular weight measurements, thermal and rheological analyses, image analysis of sections and SEM fractography. These techniques revealed a lower molecular weight, lowering of glass transition temperature, reduction of fibre length, and separation of fibre bundles with injection cycles. Nevertheless, the property retention after three cycles under extreme recycling conditions (100% recycling with no added virgin polymer) indicate the promising recyclability of these materials.

Keywords: A. Composite; A. PLLA; A. Flax fibres; E. Recycling; B. Mechanical properties

1. Introduction

Increasing environmental consciousness in the composite industry has led to a need for waste management solutions. As a result biocompostable composites are being increasingly studied, and their development must take into account environmental impact at each step of their life (from cradle to grave). When mixed together, natural fibres and biopolymers create materials known as biocomposites [1-5]. Each component comes from renewable resources and is compostable. Moreover, the use of renewable resources makes energy savings possible [6-9]. Besides biodegradation, composite recycling could make these materials more interesting and extend their useful life, reducing the global impact on the environment by minimizing raw material consumption and storing carbon for a longer period. Flax fibre reinforced poly(L-Lactic acid) (PLLA) is one of the more interesting biocomposites in terms of mechanical properties. Bodros et al [10] have shown that the specific tensile strength of this combination is higher than that of flax reinforced unsaturated polyester composite, and its specific elastic modulus is as high as that of traditional glass fibre reinforced unsaturated polyesters.

Recycling involves mechanical and thermal degradation of both the matrix and the reinforcement. For the matrix of interest here, PLLA, Pillin et al [11] studied thermo-mechanical effects of recycling on the mechanical properties, noting a reduction of stress and strain at break whereas Young's modulus remained constant. Degradation of PLLA can be catalysed at transformation temperature by the presence of air and random chain scissons occur [12]. The structure of semi-crystalline polymers such as PLLA will also evolve during multiple injections, crystallization occurs during cooling and this may be enhanced if a reduction in molecular weight results in greater mobility of molecular chains. In comparison, the crystallinity of polypropylene (PP) in Hemp/PP and Sisal/PP composites does not evolve significantly when these materials are subjected to several injections [13].

Concerning the reinforcement, natural fibres have limited thermal stability. Gassan et al [14] demonstrated that onset of thermal degradation of flax and jute fibres occurs around 170°C. When exposed to air above this temperature, there is depolymerization of the cellulose chains of flax fibres [15], even though it requires 2 hours at 210°C to reduce their strength by 70%.

In composites the mechanical properties of Sisal/PP and Hemp/PP have been investigated as a function of recycling cycles by Bourmaud et al [13]. Both tensile modulus and strength were shown to be quite stable after up to 7 injection cycles, but the initial value was quite low due to the relatively poor mechanical properties of PP. Many authors [16-18] have noted a large reduction in fibre length during multiple injection cycles. The reduction of dimensions is attributed to shear stresses developed in the injection equipment. Thompson et al [19] have studied the rheological behaviour of nanofiller/elastomer composites during recycling. Reduction of viscosity during injection cycles was caused by thermo-oxidative degradation, and destruction of filler networks was highlighted. Reduction of viscosity during injection cycles can be caused by matrix degradation (chain scissions) and/or reduction of reinforcement size.

The aim of the present work was to study the recyclability of flax/PLLA biocomposites elaborated with the injection moulding process, and to compare their behaviour with that of PP (polypropylene) composites. Recycling of biocompostable materials limits their environmental impact, while keeping possible waste management by composting. PLLA reinforced with two flax fibre contents was investigated. Tensile testing was used to follow mechanical properties, and a range of complementary analyses allowed the physico-chemical characteristics of the material to be followed after each injection cycle.

2. Materials and methods

2.1. Material

The material studied is based on a commercially available poly(L-Lactic acid), PLLA grade L9000 from Biomer®, and flax fibres, the Hermes flax variety cultivated in Normandy (France). PLLA has initially a molar mass of 220000 g/mol. The flax was dew-retted before being stripped and finally combed. The flax fibres were cut to 4 mm length. Two series of biocomposites were prepared, containing 20% and 30% by weight of fibres, and these will be referred to subsequently as BC-20% and BC-30%.
The mechanical results for the PLLA biocomposite will be compared to results obtained previously for composites based on polypropylene (PP) matrix reinforced with either glass, hemp or sisal fibres [13]. The fibre content of the latter was 30% by weight and the fibres were around 0.5 mm long after one injection, in the same range as those measured for flax/PLLA biocomposite.

2.2. Sample preparation

PLLA pellets were dried under vacuum at 60°C for 48 hours prior to extrusion. They were then extruded with flax fibres at different fibre contents (20 and 30% in weight). Compounding was achieved in a single screw extruder at 20 rpm and with the following temperature profile : 175/180/185/ and 185°C in the nozzle. Compounded pellets were also dried under vacuum at 60°C for 48 hours. Injection moulding was then carried out on a PROXIMA Billion machine. All parameters were kept constant during recycling. Temperature profile was kept as follows : 165/170/175/180 and 180°C in the nozzle. Even though these temperatures are close to those reported by Gassan et al [14] to cause degradation of flax fibres, they are necessary to transform PLLA. Materials were injected in a mould designed to produce normalized specimens. The injection pressure was 190 bars and injection time was fixed at 0.95s. The mould temperature was maintained at 30°C. Hemp/PP and Sisal/PP were injected at 180°C using the same machine and mould, with a mould temperature of 50°C. Glass/PP specimens were injected at 220°C with the same mould temperature. Recycling experiments were carried out on 6 injection cycles.

2.3. Fibre geometry measurements (length and diameter)

Fibre dimensions were measured after each injection to obtain their average length and diameter. Flax/PLLA specimens were compressed at 185°C between glass slides in order to obtain thin films. Subsequently, fibres were photographed through a Leica optical microscope (Leica Microsystems) and the average length and diameter were measured using an image analysis software program IM 500. Each value of average length and diameter presented here was determined by measurements on at least 250 fibres.

2.4. Tensile tests

The tensile specimen is a dog-bone geometry of 200 mm length and central dimensions of 10 by 4 mm² (sample 1A according to NF EN ISO 527). Static tensile tests were carried out in a laboratory where the temperature and humidity were regulated at 23°C and 48% according to ISO 527. The loading speed was 1 mm.min^{-1}. An extensometer was used with a nominal length of 50 mm to determine Young's modulus. At least ten tests were carried out for each condition and the results were averaged arithmetically.

2.5. Differential Scanning Calorimeter (DSC)

Thermograms were obtained using a Perkin Elmer *Pyris 1* DSC. Calibration was performed with indium and tin in the temperature range (+15 to +350°C). Samples of approximately 10 mg for each condition were analysed in aluminium pans. All samples are first heated to 190°C for 3 minutes to remove thermal history, in order to examine the irreversible degradation resulting from multiple injections. All the peak temperatures measured (T_c, T_m) have an accuracy of ± 0.5°C. Non-isothermal crystallization and melting temperatures, T_c and T_m, respectively, were determined from the crystallization peak extrema in experiments at heating/cooling rates of ± 20°C/min. Subsequent melting temperatures were obtained from the melting peaks maxima measured at a heating rate of 20°C/min. Melting enthalpies were determined using constant integration limits. The degree of crystallinity (χ_c) was estimated using eq. (1) :

$$\chi_c = \frac{\Delta H_m}{\Delta H_{100\%}} \qquad\qquad (1)$$

with $\Delta H_{100\%\ crystalline}$ = 93.7 J/g presented by [20]. Melting enthalpy was corrected for fibre content.

2.6. Rheological experiments

Rheological experiments were performed at 190°C using a Gemini 2000 rheometer from Bohlin Instruments. A parallel plate geometry was used. The diameter of the plates was 20 mm and the gap was 1.7 mm. The viscosity was obtained using the shear rate gradient from 0.01 to 100 s^{-1}. The zero viscosity value was calculated using the Carreau–Yasuda model [21].

2.7. Scanning Electron Microscopy (SEM) pictures

The tensile fracture surfaces were observed in a Jeol JSM 6460LV Scanning Electron Microscope. Samples were sputter-coated with a thin layer of gold in an Edwards Sputter Coater.

2.8. Steric Exclusion Chromatography (SEC) measurements

In order to measure molecular weights, a Shimatzu LC 10AD system was used in combination with a Shimadzu RID10A differential refractometer and a Shimatzu SP 10Avp UV dual wave length detector (λ_1= 254 nm and λ_2= 280 nm). The column set consisted of five 30 cm gel columns with a granulometry of 10µm (from Polymer Laboratories). The solvent was analytical grade THF (dried on calcium hydrure) at a flow rate of 1mL/min. The SEC analyses were performed at room temperature.

3. Results and discussion

3.1. Tensile properties of injected Flax/PLLA biocomposite

Table 1 presents a comparison between the mechanical properties of the biocomposites from the present study (flax fibre reinforced PLLA matrix) after the first injection cycle, with properties of unreinforced PLLA and PP, and results from previous work on natural fibre and glass fibre-reinforced PP matrices.

Fig. 1

Results show an increase of Young's modulus when flax fibres are added (Table 1). Tensile modulus is mainly governed by the mechanical properties of the fibres. The average longitudinal tensile properties of the flax fibres used for this work are given by Charlet et al [22] : Ef_L = 65.8 ± 38 GPa , σf_L = 1455 ± 835 MPa, εf_L = 2.3 ± 0.6 %. These values are a little lower than those of glass fibres (Ef_L = 72 GPa, σf_L = 2200 MPa, εf_L = 3% [23]). The transverse modulus of flax fibres has been studied previously and found to be Ef_T = 7 ± 2 GPa [24].

It is possible to use micromechanics expressions to estimate the tensile stiffness of the flax/PLLA composite from the fibre and resin elastic properties and their proportions, and the aspect ratio L/d. The longitudinal modulus E_L and the transverse modulus E_T for a ply reinforced by short unidirectional fibres is given by equations (2) and (3) proposed by Halpin-Tsaï [25] :

$$\frac{M}{M_m} = \frac{1 + \xi \cdot \eta \cdot V_f}{1 - \eta \cdot V_f} \quad (2)$$

$$\text{where } \eta = \frac{\dfrac{M_f}{M_n} - 1}{\dfrac{M_f}{M_m} + \xi} \quad (3)$$

where M = E_L or E_T, M_f = E_{fL} or E_{fT} and m, f, L, T correspond to matrix, fibre, longitudinal and transverse. V_f is the fibre volume fraction and ξ the form factor. For the longitudinal modulus ξ = (2L/d), where (L/d) is the fibre aspect ratio (reinforcement length, L, divided by its diameter, d). For the transverse modulus (E_T) satisfactory results have been obtained with ξ = 2 [26]. The modulus of a ply reinforced by randomly dispersed fibres is then given by the following expression [26]:

$$E_{mat} = \frac{3}{8} E_L + \frac{5}{8} E_T \quad (4)$$

where E_L is the longitudinal modulus and E_T the transverse modulus of the unidirectional ply. Measured and calculated values are given in Table 2 as well as aspect ratios measured after injection.

Table 2

The results shown in Table 2 indicate a reasonable correlation between predicted and measured stiffness values, the latter being slightly overestimated by about 5%. It should be remembered however, that the quality of the interface is not taken into account in these micromechanics expressions, nor the statistical variations in aspect ratio, the fibre bundles, the exact fibre distribution nor the influence of fibre diameter on longitudinal modulus.

It may be noted that the stress at break of the matrix polymer is not enhanced by the addition of flax fibres (Table 1). In fact the neat PLLA, BC-20% and BC-30% present respectively mean stress at break of 60, 55.5 and 53.1 MPa. Strains at failure follow the same trend and decrease with increasing fibre content. The 20 wt% and 30 wt% biocomposites exhibit, repectively, strains at break of 1.4% and 1.2% compared with 2.4% for neat PLLA. Although fibres are added, injected samples do not show an increase of properties at break principally because of flax fibre anisotropy [24], strain concentrations induced by fibres, the bundle organization of fibres and the low aspect

ratio of fibres. In previous work on biocomposites with the same biopolymer and the same type of fibre a random mat reinforcement was used [10]. In that case, for biocomposites manufactured by film stacking (heating and compressing a stack of polymer films and fibre mats), mechanical properties were higher than those of the matrix polymer (Table 1). Unlike injection moulding, film stacking is a single tranformation cycle process and does not need a preliminary compounding step. Thus fibres are not subjected to length reductions. During injection fibre length reduction is very large, from an initial value of 4 mm before extrusion, to 2.7 mm before injection and to around 0.33 mm after injection, as will be shown below. Flax fibres used in the film stacking method were also initially longer than those for the injection moulding process (10 mm). Fig. 2 shows stress-strain curves of injected biocomposite and injected natural and glass fibre reinforced PP. All the materials have the same reinforcement content (30 % by weight) and the same range of fibre length after one injection (around 0.5 mm)[13].

Fig. 2

Flax/PLLA biocomposite and glass/PP composite have similar tensile stiffness while the modulus of hemp/PP and sisal/PP composites is around half this value (Table 1). The brittleness of the biocomposite (as a result of the low failure strain of PLLA) is also shown in Fig. 2. The tensile strength at yield of flax/PLLA biocomposite is lower than that of glass/PP (Table 1) but higher than that of the hemp and sisal/PP composites. Hemp and sisal fibres have been shown previously to have lower mechanical properties than those of flax [27].

In this first section the properties of flax/PLLA biocomposites have been shown to be very promising when compared with several other thermoplastic composites, even though their mechanical properties are strongly dependent on the processing route. In the next section the recyclability of the biocomposite will be described.

3.2. Recycling investigation of flax/PLLA biocomposite

3.2.1. Evolution of reinforcement geometry with injection cycles

Reinforcement aspect ratio is an important parameter for composite reinforcement. Table 3 presents the evolution of this parameter as a function of injection cycle for flax fibres.

Table 3

The results show a large drop in aspect ratio (L/d) during the first injection. However, in subsequent cycles 1 to 6 this ratio decreases little, remaining in the same range of values as can be seen for the example of BC-20% (Fig. 3). Initially the plant fibres are organised in bundles. During injection the fibre length will be shortened but bundles will also be sub-divided into single fibres, reducing the global measured diameter of the reinforcement.

Fig. 3

These modifications to the reinforcement geometry are linked with shear rate generated in the process, and depend on rotation speed of the screw, pressure and barrel temperature. Extrusion and injection moulding involve respectively a reduction of about 20% and 70% compared to initial fibre diameter.

3.2.2. Evolution of tensile fracture surfaces examined by SEM

Observation of tensile fracture surfaces in the SEM gives qualitative information about fibre dispersion and orientation. After the first injection cycle many bundles of fibres can be noted (Fig. 4) and thus a lack of homogeneity compared to the fracture surface of a sample subjected to 6 injection cycles (Fig. 5).

Fig. 4   Fig. 5

This confirms bundle division during recycling, and can explain the small change in fibre aspect ratio with injection cycles.

3.2.3. Tensile properties.

Table 4 shows the evolution of mechanical properties of flax/PLLA biocomposites for two fibre contents (20 and 30w%) during recycling.

Table 4

Tensile modulus is only slightly influenced by recycling as illustrated in Fig. 6. This trend was also noted during previous tests on hemp and sisal/PP composites [13]. A small reduction of PLLA modulus during recycling, shown by Pillin et al [11] is one of the reasons for this behaviour. Another is the small decrease of fibre aspect ratio during recycling.

Fig. 6

Fig. 7   Fig. 8

Fig. 7 and 8 show that, for both fibre contents, Stress and strain at break decrease. This drop may be caused by fibre damage during recycling, the reduction in fibre length results in more strain concentrations and a higher risk of debonding. Par ailleurs en comparant ces résultats à la matrice pure [11], on note que le biocomposite suit une tendance analogue, reliant ainsi l'impact de la dégradation de la matrice sur les propriétés à rupture du composite. L'analyse de la dégradation de la matrice et du composite via l'étude des masses molaires est abordé dans la partie suivante.

Although biocomposites become more brittle with recycling (Fig. 8), they retain a large part of their properties, at least until the third injection cycle. Moreover one should keep in mind that in an industrial situation, 100% of recycled biocomposite would not be used, (recycled material is always mixed with virgin material).

In a similar way to that described previously, the modulus of biocomposites can be estimated with number of injection cycles using the micromechanics expressions presented above. The aspect ratios are given in Table 3. PLLA modulus values are taken from the study of Pillin et al [11].

Results in Table 5 show that the evolution of the biocomposite stiffness can be quite accurately predicted, given the simplifying assumptions of the expressions employed.

3.2.4. Influence of recycling on molecular weight of PLLA

In the previous study on recyclability of this PLLA grade [11] tensile modulus was nearly constant during recycling, but a drop of stress at break was noticed. Indeed, after 6 cycles tensile stress at break was equal to a third of the initial value. In order to examine the matrix degradation mechanism molecular weight of PLLA was investigated as a function of injection cycles. Fig. 9 shows the evolution of molecular weight for the biocomposites at different fibre contents compared to neat PLLA. Initially molecular weight of PLLA was 220000g/mol (supplier's data).

Fig. 9

During multiple injections molecular weight of PLLA decreases dramatically. Fibre content play an important role in reduction of molecular weight of polymer, since the higher the fibre content the more rapidly molecular weight decreases (-83% for BC-20% and -94% for BC-30%). The chemical structure of PLLA is sensitive to hydrolytic degradation and especially to high temperature [11], [28]. Water contained in flax fibers and high process temperatures will provide favourable degradation conditions. Other kinds of degradation process will also occur during recycling : depolymerisation of macromolecular chains due to residual catalyst, radical and nonradical reactions, cis-elimination, trans-esterification [28-29], and mechanical degradation due to interactions of the polymer with the equipment and high shear rate in the injection process. An increase of fibre content leads to higher shear rates. Complex degradation processes result in molecular weight reduction during recyling. The drop in PLLA molar mass will directly influence the flax/PLLA biocomposite properties et plus spécialement leurs propriétés à rupture.

3.2.5. Calorimetric properties

Fig 10 and 11, obtained by DSC, show the influence of injection cycles on glass transition temperature (T_g) and melting enthalpy (ΔH_m) of the PLLA and the biocomposites BC-20% and BC-30%. All the data are indexed in Table 6.

<center>Fig. 10   Fig. 11</center>

During the first injection, the presence of fibres causes little change in glass transition temperature (T_g) (Fig. 10). These results are confirmed by the work on injected, recycled newspaper fibre/PLLA biocomposites of Huda et al [30]. Addition of 20 wt% fibre content does not modify crystallization enthalpy significantly. BC-20% behaves like neat PLLA, i.e. it crystallizes in a metastable way (cold crystallization) (Table 6). After the first injection BC-30% crystallizes during cooling, and its degree of crystallinity increases from 39 to 47% compared to neat PLLA. (Table 6). Although several authors [31-33] have affirmed the nucleating role of natural fibres in matrix polymers, the results here do not allow this to be confirmed. Indeed, an increase in crystallinity can also be explained by the higher chain mobility resulting from more severe degradation in the case of composites. This is confirmed by molecular weight measurements. During recycling, T_g of both BC-20% and BC-30% are reduced by approximately 6°C and 20°C respectively after 7 injections (Table 6). This tendency represents an increase in macromolecular chain mobility that can be due to chain scission mechanisms as well as reduction of fibre geometry during mechanical recycling. An analogy can be observed between the evolution of melting enthalpy of the PLLA and the BC-20% (Fig. 11). The BC-20% behaviour is similar to that of PLLA with a constant increase of melting enthalpy as a function of injection cycles. The melting enthalpy of BC-30% increases until the 3rd cycle and then decreases slightly to drop at the 5th cycle. Evolution of ΔH_m of BC-20% can also be explained by degradation induced during recycling. Shorter chains will be able to move more easily and will thus facilitate crystallization mechanisms.
The results (Table 6) also show that BC-20% crystallizes in a metastable way after the first injection. During recycling, this behaviour tends to be reversed. Indeed during the second injection a crystallization peak appears during cooling (whose enthalpy increases as a function of injection cycles), while cold crystallisation tends to decrease. This observation supports the assumption of PLLA degradation. After the first injection, BC-30% crystallizes completely on cooling. Its enthalpy of crystallization increases

slightly until the 4th cycle. From the 5th cycle a cold crystallization peak appears and tends to increase with the following cycles whereas the peak of crystallization during cooling decreases

If we consider that BC-30% crystallizes directly on cooling because it is more degraded than BC-20% (thus the chains are shorter), this does not explain why a cold crystallization peak appears after the 5th cycle. Moreover neither SEC analysis, nor the mechanical tests show any variation. We still have no clear explanation of this phenomenon, but it may be that from the 5th cycle the molecular weight of the PLLA reaches a limiting value which makes the crystallization mechanism harder.

Table 6

3.2.6. Rheological properties

Fig. 12 presents the evolution of Newtonian viscosity (η_0) as a function of the number of recycling processes for the PLLA, BC-20% and BC-30%.

Fig. 12

During the first injection, it may be noted that for higher fibre content, the viscosity is higher. Several authors have noted that as fibre content increases chain mobility of PLLA is restricted, this may be due to the fibre-polymer and fibre-fibre interactions [34-37]. During recycling, the viscosity of BC-20% and 30% decrease (Fig. 12). This viscosity drop, either for PLLA, BC-20% or BC-30%, is very significant, indicating a high degradation rate of the PLLA matrix. Molecular weight reduction (also shown by SEC), reduction of fibre length and aspect ratio are the phenomena that explain this observation. Several authors have described the influence of the length and L/d ratio of fibres on the viscosity of composites [34, 38].

4. Conclusion

The purpose of this work is to study the recyclability of biocompostable flax fibre reinforced PLLA composites with two fibre contents. Mechanical, thermal and rheological properties of flax/PLLA biocomposites have been investigated. The evolution of matrix molecular weight and reinforcement geometry during recycling have also been studied.

First it has been shown that the mechanical properties of biocomposites are very interesting compared to those of currently used industrial thermoplastic composites (hemp/PP, sisal/PP and glass/PP). Initial stiffness can be predicted using the Halpin-Tsaï. micromechanics expressions.

Repeated injection cycles are shown to influence many parameters such as :

- Reinforcement geometry. A low evolution of reinforcement aspect ratio was observed due to a combination of length reduction and bundle division.

- Mechanical properties. Young's modulus of biocomposites shows a slight reduction but a large drop is observed in stress and strain at break with recycling. A small decrease of PLLA modulus shown previously [11], and a low evolution of the aspect ratio, explain the small change in biocomposite modulus. La forte réduction des propriétés à rupture de la matrice pure induite par les multiples injections sont responsables de la diminution de la contrainte de l'allongement à rupture du biocomposite . Higher fibre content is shown to have an adverse effect on mechanical properties at failure of biocomposites, owing to

strain concentrations and higher shear rate during processing. Micromechanics expressions give a satisfactory estimation of the evolution of modulus with injections.

- Molecular weight of PLLA. A drop in PLLA molecular weight is observed as fibre content and number of injection cycles increase. Higher fibre content appears to accelerate PLLA degradation during recycling. La réduction de la masse molaire de la matrice PLLA au cours des injections joue un rôle dans la diminution des propriétés à rupture du biocomposite.

- Thermal behaviour. Calorimetric study shows that, depending on fibre content, glass transition temperature decreases and degree of crystallinity increases with injection cycles. This evolution can be explained by degradation during processing which induces higher molecular mobility.

- Rheological behaviour. Newtonian viscosity of these biocomposites decreases as a function of injection cycles. This emphasizes the degradation of the matrix (reduction of molecular weight) through chain scission mechanisms during recycling. η_0 reduction can also be explained by a decrease of fibre length.

To summarize, biocomposites exhibit interesting recycling properties, especially if we consider that in the industrial process recycled material would include both virgin and recycled matter. Furthermore, with natural fibres as reinforcement end-of-life composting is possible.
Complementary work on degradation mechanisms and their link to environment (temperature, humidity…), as well as detailed damage threshold identification are in progress.

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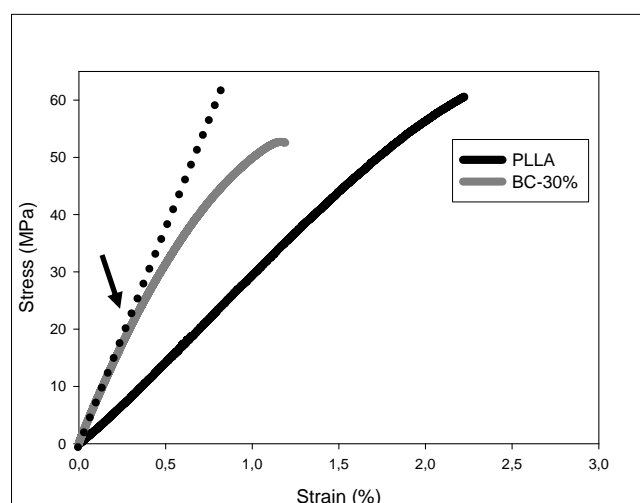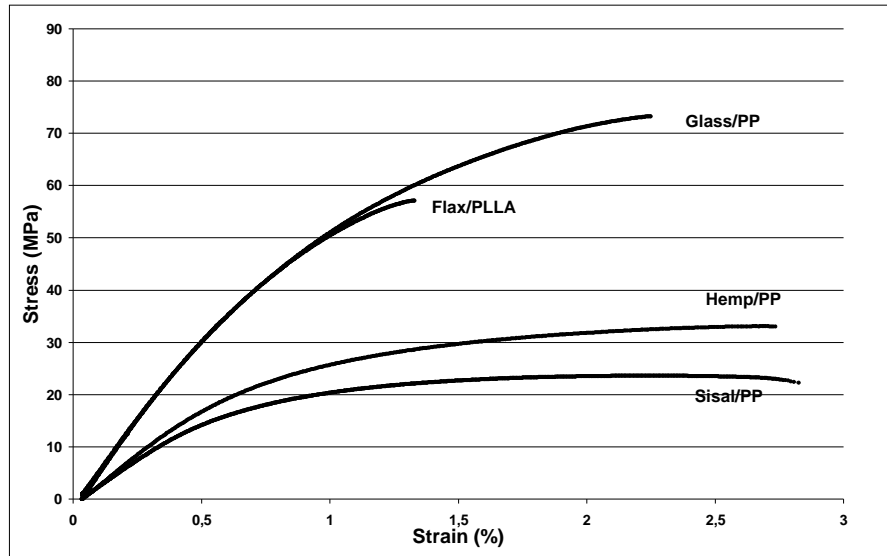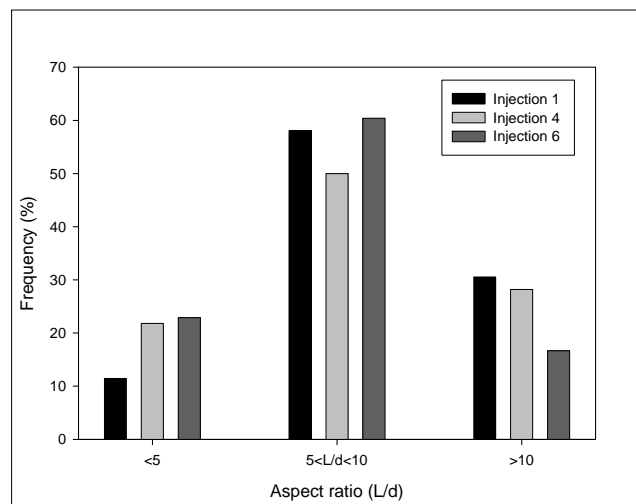
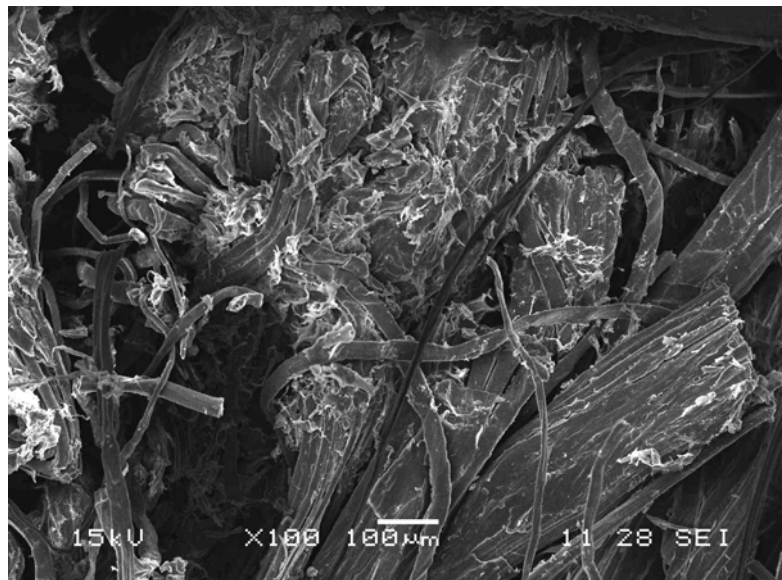## Acknowledgements

Figures

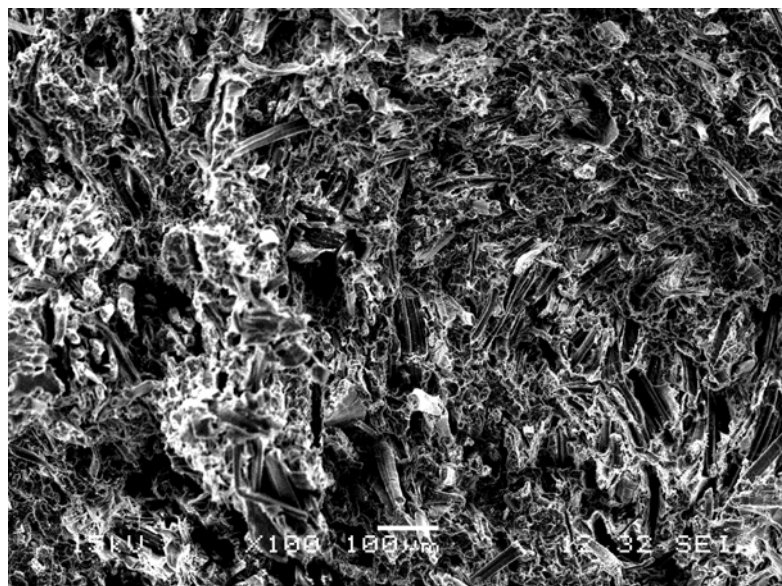**Fig. 1. Stress-strain curves of PLLA and BC-30%**

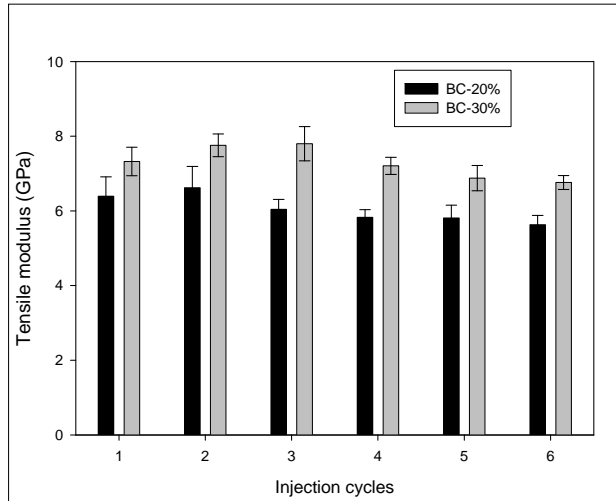**Fig. 2. Stress-strain curves of biocomposite compared to other thermoplastic composites**

Fig. 3. Evolution of fibre aspect ratio distribution of BC-20% as a function of injection cycles
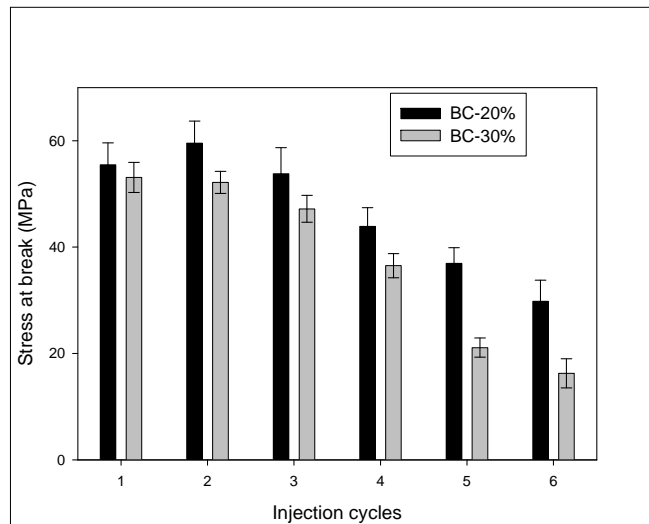
**Fig. 4. SEM micrograph of the fracture surface
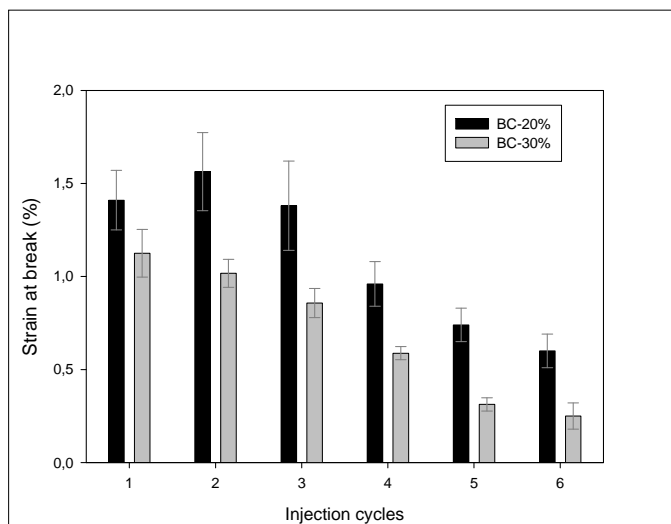of BC-20 after 1 injection**

**Fig. 5. SEM micrograph of the fracture surface
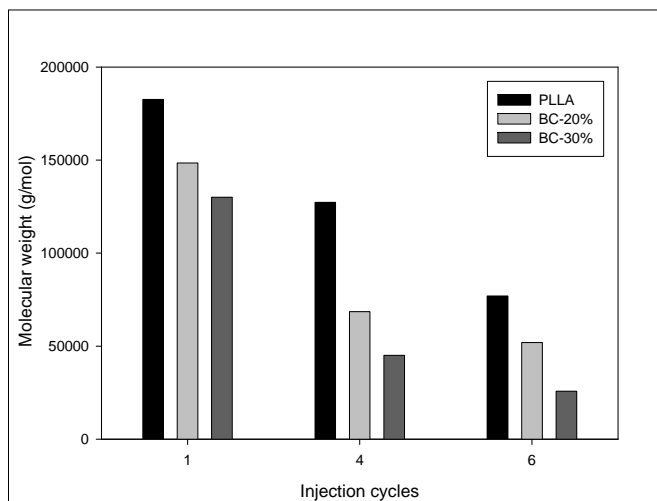of BC-20% after 6 injections**

Fig. 6. Evolution of tensile modulus as a function of injection cycles

Fig. 7. Evolution of stress at break as a function of injection cycles

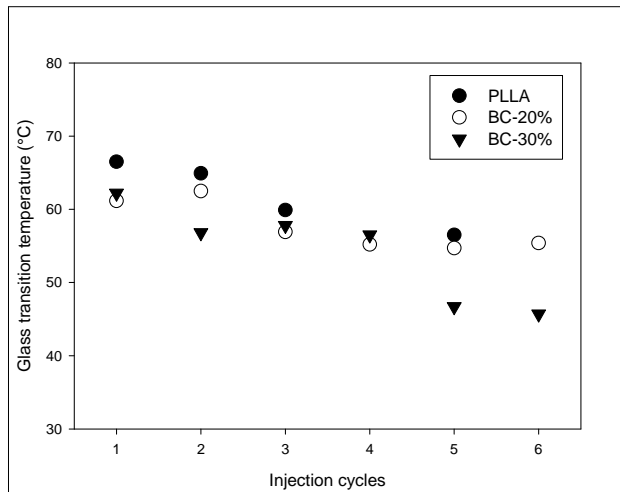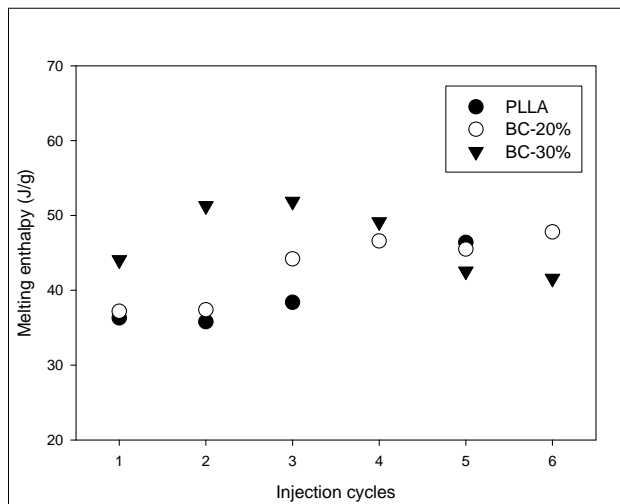**Fig. 8. Evolution of strain at break as a function of injection cycles**

Fig. 9. Evolution of molecular weight as a function of injection cycles
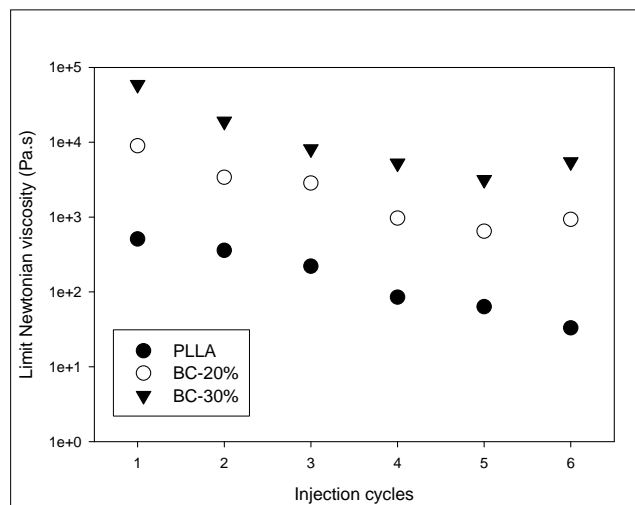
Fig. 10. Evolution of glass transition temperature as a function of injection

Fig. 11. Evolution of melting enthalpy as a function of injection cycles

Fig. 12. Evolution of Newtonian viscosity as a function of injection cycles

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Tables

Material	Process	Fibre content (w%)	Fibre content (v%)	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Ref.
PLLA	injection	/	/	3620± 67	60.1 ± 1.7	2.4 ± 0.4	
Flax/PLLA	injection	20	17	6395 ± 515	55.5 ± 4.1	1.4 ± 0.1	
	injection	30	26	7320 ± 380	53.1 ± 2.8	1.2 ± 0.1	
	Film-stacking	30.5	25	8856±297	81.3±7.7	1.2± 0.1	[10]
Flax/PLLA	compression	30		8300 ± 600	53 ± 3.1	1.0 ± 0.2	[2]
Flax/PLLA	injection		20	6197	64.4	6.21	[39]
PP	injection	/	/	1660 ± 30	26.1 ± 0.4	148 ± 3.6	[13]
Hemp/PP		30		3800 ±180	33.1 ± 0.2	2.8 ± 0.1	
Sisal/PP		30		3500 ± 70	23.3 ±0.3	2.8 ± 0.3	
Glass/PP		30		6800 ± 170	73.3 ± 0.6	2.4 ±0.2	

Table 1 Tensile properties of Flax/PLLA biocomposites compared to other thermoplastic composites

Material	Fibre content V_f (%)	$E_{mesured}$ (MPa)	L/d	$E_{estimated}$ (MPa)
BC-20%	17	6395 ± 515	9,3	6624
BC-30%	26	7320 ± 380	9,1	7740

Table 2 Tensile properties of biocomposites, measured and estimated with micromechanics expressions (Eq. 2, 3, 4)

Material		Mechanical properties after 1 cycle	Mechanical properties after 6 cycles	Evolution of mechanical properties from cycle 1 to cycle 6 (%)
PLLA	E (MPa)	3620± 67	3518 ± 192	-2,8
	σ (MPa)	60.1 ± 1.7	27,8± 8,9	-53,8
	ε (%)	2.4 ± 0.4	0,9 ± 0,4	-72,5
BC-20%	E (MPa)	6395 ± 515	5633 ± 247	-12,0
	σ (MPa)	55.5 ± 4.1	29.8 ± 3.9	-46.3
	ε (%)	1.4 ± 0.2	0.7 ± 0.1	-47.6
BC-30%	E (MPa)	7320 ± 380	6760 ±183	-7.7
	σ (MPa)	53.1 ± 2.8	16.3 ± 2.7	-69.4
	ε (%)	1.1 ± 0.1	0.2 ± 0.1	-77.7

Table 3 Average geometry data for BC-20% and BC-30% as a function of injection cycles

Injection cycles	Fibre content (w%)	Length (µm)	Diameter (µm)	Aspect ratio (L/d)
Without extrusion	/	4064 ± 670	182 ± 76	25.8 ± 11.1
After extrusion	20%	2697 ± 1258	149 ± 66	20.7 ± 12.2
	30%	2319 ± 1242	133 ± 60	19.8 ± 13.8
1	20%	420 ± 398	52 ± 45	9.3 ± 6.6
	30%	334 ± 277	44 ± 42	9.1 ± 5.8
3	20%	255 ± 94	35 ± 13	8.8 ± 3.9
	30%	208 ± 71	25 ± 5	8.3 ± 4.3
6	20%	124 ± 55	18± 7	6.9 ± 2.7
	30%	114 ± 65	17 ± 7	6.5 ± 2.4

Table 4 Evolution of mechanical properties of Flax/PLLA biocomposites at different fibre contents during recycling.

Material	Injection cycles	Fibre content Vf(%)	$E_{measured}$ (MPa)	L/d	$E_{estimated}$ (MPa)
BC-20%	1	17	6395 ± 515	9,3	6224
	3		6097 ± 211	8,8	6184
	6		5633 ± 247	6,9	5801
BC-30%	1	26	7320 ± 380	9,1	7740
	3		7210 ± 128	8,3	7624
	6		6760 ± 183	6,5	7110

Table 5 Evolution of measured and estimated Young's modulus (Eq. 2, 3, 4)

Material	Injection cycles	T_g (°C)	1rst cooling		2nd heating				
			T_c (°C)	ΔH_c (J.g^{-1})	T_c (°C)	ΔH_c (J.g^{-1})	T_m (°C)	ΔH_m (J.g^{-1})	χ (%)
PLLA	1	66.5	/	/	123.3	36.5	175.1	36.3	38.7
	3	59.9	93.6	15.9	104.3	16.4	171.1	38.4	41.0
	6	56.5	97.7	38.9	89.8	0.6	167.3	49.9	53.2
BC-20%	1	61.1	/	/	110.9	36.5	170 .7	37.2	39.7
	3	56.9	89.1	16.8	90.4	21.6	167.4	44.2	47.1
	6	54.9	92.4	41.3	/	/	163.9	47.1	50.2
BC-30%	1	62.2	114.5	45.6	/	/	170.4	44.0	47.0
	3	57.8	112.5	45.6	/	/	163.4	51.9	55.3
	6	41.7	87.1	35.9	85.1	5.1	152.3	40.2	43.2

Table 6 Evolution of thermal properties of PLLA, BC-20% and BC-30% as a function of injection cycles. T_g, T_c, ΔH_c, T_m, ΔH_m and χ represent respectively the glass transition temperature, the crystallization temperature, the crystallization enthalpy, the melting temperature, the melting enthalpy and the degree of crystallinity.