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Innovating routes for the reused of PP-flax and PP-glass non woven composites: A comparative study

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A B S T R A C T

The significant industrial development of non-woven biocomposites requires the implementation of environmentally and economically coherent end-of-life recycling solutions. In this study, we studied the recycling of a non-woven poly-(propylene)-flax composite by injection but also by thermo compression. For comparison, a material with the same architecture but reinforced by glass fibres was studied. Both recycling methods showed strong specificities. Injection recycling leads to efficiently homogenised microstructures of the parts but also to drastically reduced lengths of the fibres, up to 10 times lower than with compression moulding. This method globally promotes high failure strengths while compression moulding, by preserving the length of the fibrous reinforcements, guarantees higher stiffness. This work also highlights the impacts of the length and division of the fibre elements on the microstructure of the injected parts; thus, after a series of compression recycling cycles, injected parts exhibit an important skin-core effect larger than after initial injection recycling cycles, whether in terms of orientation or local fibre volume fraction. As a consequence, after a series of recycling by compression, a new injection cycle has for effect to improve the tensile mechanical performances. For example, the strength and modulus of PP-flax composites are increased by 103% and 75%, respectively. These results highlight the technical feasibility and relevance of implementing these two recycling methods, depending on the volumes or equipment available and the final properties to promote, as they enable the production of new high-performance parts.

Keywords:

Flax fibre
Recycling
Non-woven
Mechanical properties
Tomography
Fibre length

1. Introduction

The end of life of composites is a major issue for this industry and the depletion of fossil resources requires producers to promote the recycling of parts after use. Some sectors, such as the automobile, have implemented drastic regulations to comply with standards and European directives [1] that promote end-of-life treatment through the recyclability of materials [2–4]. In response, the design of mechanically recyclable composites involves the development of thermoplastic matrices instead of thermoset resins [5].

Currently, many researches and industrial developments dealing with the use of natural fibres to substitute glass fibres in some applications are conducted. Indeed, they are produced from renewable resources, need 5 to 10 times less non-renewable energy, have a low density inducing interesting specific mechanical performances [6] and are able to store carbon dioxide thanks to photosynthesis [7,8]. These factors contribute to a great reduction of the environmental impact during car manufacturing and use [9]. In Europe, flax and hemp are the most frequently used natural fibres due to their high specific mechanical properties [6,10,11] and moderate cost. European production land reaches 114.000 ha per year and France grows 75% of the European flax fibre (2001–2008), being thus the first worldwide producer. When these plant fibres are associated with bio-based or biodegradable matrix such as PLLA/PHB alternative end-of life routes such as composting [12,13]

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can be carry out. However, those matrices are not easily usable in automotive applications due to their low thermal stability, low tenacity and high price. For these reasons PP is often preferred because of its good mechanical property and chemical stability [14,15].

In this context, the use of compression moulded non-woven PP-flax biocomposites is greatly appreciated in vehicle manufacturing (mainly in car interior parts); these materials offer a short time process cycle, limited raw material cost [16] and they can potentially offer both sound absorption (thanks to porosities) and good mechanical properties [17]. It is possible to vary their porosity in a range from 5 to 60%, so that to obtain configurable materials, covering a large panel of applications. If a 60% porosity content appears to be ideal to reach good absorption performance, in this case, the mechanical properties, for a fibre fraction of 40%-vol, dropped drastically from $E_{0\%} = 6$ GPa to $E_{60\%} = 1$ GPa and $\sigma_{0\%} = 40$ MPa to $\sigma_{60\%} = 10$ MPa for the tensile modulus and maximal stress, respectively. In the automotive sector, non-woven use is divided fairly between glass and plant fibres. Mechanically speaking, literature shows that non-woven composite moduli are generally included between 5 and 7 GPa for both low porosity PP glass or flax non wovens [18–20]. The strength at break is generally higher when glass fibre is used [18,20]. Interestingly, when maleic anhydrid grafted PP (PP/PPgMA) is used modulus and strength at break of flax composites are highly improved reaching 9.5 Gpa and 95 MPa [18,19,21], respectively.

The main drawback of non woven composite manufacturing is the waste production because ~25%wt of the used semi-product is thrown away. Due to the previously described advantages of plant fibres and the necessary need to value the non wovens wastes, recycling is a preferable alternative to incineration and landfilling because it helps to dispense with all or part of production phase [22], save raw material and a level of performance can be maintained. A viable solution could be the reutilisation of these wastes for injection moulding which is the most common way to recycle such products. Biocomposites showed that they may exhibit an interesting recycling behaviour characterised by successive process cycles inducing only few modifications in tensile modulus and strength values for vegetal fibres whereas for glass fibres the decrease was very substantial, particularly with a stable PP matrix [23–25]. This phenomenon is mainly explained by the evolution of fibre length but also by the poor adhesion between glass fibres and matrix after several cycles.

In addition to fibre length or microscopic analysis, it is possible to deeper investigate the composite by using tomography or micro-tomography which are powerful tools to explore microstructure of plant fibre bundles [26,27] but also to investigate structure or damage in plant fibres composites. Thus, the fibre-bundle structure within a composite can be studied through tomography for modelling investigations [28]. Moreover, Almansour et al. [29] and Rask et al. [30] used tomography to investigate damages within flax/basalt vinyl ester hybrid composites and PP-flax UD composites, respectively, without any alteration of the composite structure as it is the case for SEM observations, for example. Tomography is also commonly used to better know the fibre orientation and porosity content within injected composite as demonstrated by Martin et al. [31] on PP-flax or Albrecht et al. [32] on PP-sisal materials.

In a previous study [33], two innovative routes for flax non wovens recycling were explored; a first one consists in introducing ground wastes in injectable compounds and the second one consists in the reintroduction of these shreds in new-non wovens. It was proved that this incorporation was structurally and mechanically successful until a reincorporation rate of 40%-wt. The aim of the present paper is to explore a new recycling possibilities,

representing an important issue for these kind of products.

The recycling of PP/flax or glass non wovens was firstly investigated by carrying out four successive injection cycles without any compounding stage. The evolution of the fibre length as well as the evolution of the rheology, the mechanical properties and the microstructure of injected samples were monitored all along the cycles. Both tomographic and SEM analysis were performed to analyse the microstructures of the successively recycled parts. The results were compared to another way of recycling inspired from the manufacturing of chopped tapes by compression moulding. The interest of this process is to combine the advantages of using centimetre fibre length (on the contrary to injection moulding that uses millimetric fibre length) and the possibility to manufacture complex shapes [34–41].

However, instead of using chopped tapes, this work proposes to use composite manufactured flat parts as initial raw material to mimic the use of composite production scraps or composites at the end of their life. The process consisting of compressing centimetric piece of an initial composite (with a defined or a random shape) is used in this context as a recycling technique. The main challenge here consists of using pieces of composite initial materials that are initially in a hard form on the contrary to the chopped tapes. Moreover, these pieces of composites possess initial thicknesses that are much higher than the chopped tapes and one can expect that the flow and the rearrangement of the pieces of composites arranged randomly in the mould with a defined covering factor do not behave in the same manner as with chopped tapes. It is therefore proposed in this work to compare this innovative recycling route using centimetric pieces of composites (with therefore centimetric fibre lengths) to a direct injection moulding recycling route (without any addition of fresh polymer) during four successive recycling steps.

More precisely, after compression moulding, non-woven plates were specifically cut and successively hot pressed. Three compression cycles were carried out before a final injection cycle. The two recycling routes were compared through mechanical and structural investigations.

2. Experimental section

2.1. Materials

Flax tows (*Linum usitatissimum*) were used as reinforcement fibres and cultivated in Normandy area (France) in 2014. They were combined with black polypropylene fibres to manufacture commingled nonwoven according to the carding/cross lapping/needle punching technology developed by EcoTechnilin® SAS (Valliquerville – France). Recycled E-glass fibres were also combined with polypropylene to manufacture a second nonwoven. The fibre-matrix ratio is 50-50%wt and areal weights were 2290 g/m² and 2000 g/m², respectively for PP/flax and PP/glass nonwovens. Moreover, the nonwoven reinforcement is considered quasi-isotropic [42]. The melt flow index (MFI) of the non-woven PP is 25 g/10 min (at 190 °C and under a load of 2.16 kg).

2.2. Nonwoven plates compression moulding for injection moulding and compression moulding recycling cycles

Commingled PP/flax and PP/glass nonwovens were produced by hot compression moulding for injection moulding recycling cycles. A LabTech Scientific 50 T hydraulic press was used to manufacture plates with a porosity content as close as possible to zero. They were obtained by setting the plate thickness to a constant value (3.5 mm) and stacking two nonwoven plies. The plies were hot pressed at 200 °C and 20 bars during 8 min. The product was then

cooled down between two trays (15 °C/min and 20 bars) during 4 min.

Non-woven composites were also produced with a hydraulic press PEI LAB 800 P for compression moulding recycling cycles using one PP/flax and two PP/glass nonwoven plies with a porosity content as close as possible to zero. Plies were hot pressed at 200 °C and 25 bars during 10 min then cooled down at 10 °C/min until demoulding. The resulting thickness was about 1,8 mm.

2.3. Recycling process

Fig. 1 schematises the two valorization routes studied in this paper. Two main axis were defined.

Firstly (axis 1), the obtained plates (see 2.2 section) were considered for compression moulding recycling cycles. Three compression moulding recycling cycles were performed for each PP/flax and PP/glass materials. As for the manufacturing of the initial composite plate, non woven composites were produced with the hydraulic press PEI LAB 800 P. After each cycle, one part of the samples was cut (25 × 25 mm) for a new compression moulding recycling cycle using a pressure of 50 bars. The first recycling was performed with a mass equivalent of 2,5x the initial plate, second recycling with +15% and third recycling with another +15% of cut materials. In all case, the materials were uniformly spread into the mould with a covering factor of about 75% in order to have a random and uniform dispersion within the final plate. The other moulded samples were kept for analysis. To be consistent and comparable with the four injection cycles, the plates were granulated through a CMB 2700 rotary blades grinder (3.5 mm) and a last recycling cycle was performed with an injected normalised samples for each material (same parameters as in the following paragraph).

Secondly (axis 2), non woven plates were granulated through a CMB 2700 rotary blades grinder (3.5 mm). The granulated materials were injected in a mould to form ISO-527-2 normalised samples by a Battenfeld 80 tons machine with a mould temperature of 40 °C and a barrel temperature of 200 °C. The first cycle, the injection pressure, holding time and switching pressure were 1800 bars, 10 s

and 1500 bars. For the next steps, the temperature profile was maintained and the previous parameters were changed to 1600 bars, 10 s and 1400 bars respectively. After each cycle, one part of the samples was ground for a new injection cycle. The other injected samples were kept for analysis. Four injection cycles were performed for each PP/flax and PP/glass material.

All the materials were dried at 60 °C during 15 h before injection and compression moulding.

2.4. Fibres morphology measurements

For each raw material (PP/flax and PP/glass nonwovens) granulates and after every injection cycle (including the last injection in compression moulding way), the fibre elements length, diameter and aspect ratio (ratio of length to diameter) were quantified. The tests, for injection parts, were made in the middle of ISO-527-2 normalised samples. After a PP matrix extraction step by pyrolysis (700 °C during 30 min) for the glass fibres and a dilution into boiling xylene (150 °C during 48 h) for the flax fibres, the morphology was determined using a trinocular magnifier Leica MZ16 by analysing the images with the IM500 software. Length and diameter of around 200 fibres were measured for each sample. Analysis were also performed using the same approach after the third compression moulding cycle.

2.5. Structural characterisation

2.5.1. SEM analysis

SEM analysis was performed on injected composite samples (at the first and last recycling) after inclusion in an epoxy resin pad and cross sections were analysed after a meticulous polishing up to 3 µm particle size. Samples were sputter-coated with a thin layer of gold in an Edwards Sputter Coater and analysed with a Jeol JSM 6460LV electron scanning microscope at 20 kV.

2.5.2. Tomographic investigations

Volume images were generated by using a laboratory tomography device (Easytom RX Solution). A tension of 100 kV and an intensity of 100 µA were used as acquisition parameters. Specimen were positioned on a rotation stage and 1440 projections of transmitted X-ray intensity field were recorded at each angular step of 0.25° by a flat panel detector (1920 × 1536 pixels) through an X-ray detector (Fig. 2). Each projection is obtained by averaging ten images recorded at the same angular position.

A volume image of the variations of the linear attenuation coefficient in the specimen was reconstructed from all radiographies by using a filtered back-projection algorithm. The distribution of grey levels in 3D images is due to local differences of density and so corresponds to a 3D representation of the microstructure of the studied specimen. Each volume image is reconstructed with the same voxel size of 20 µm.

2.6. Tensile characterisations

Static tensile tests were performed on a MTS Synergie RT/1000 tensile machine equipped by a 10 kN load cell and a 25 mm nominal length extensometer at a crosshead displacement speed of 1 mm/min. The values presented in this paper are average values of five reproducible tests, according to ISO-527-2. The compression moulded composite samples were machined from a plate into normalised dumb-bells using a 3-axis CNC milling machine. Prior to tensile experiments, both injected and machined samples were conditioned one week at 23 °C and constant humidity of 48% RH. Average tensile modulus, strength and strain at break were measured from at least 5 reproducible samples.

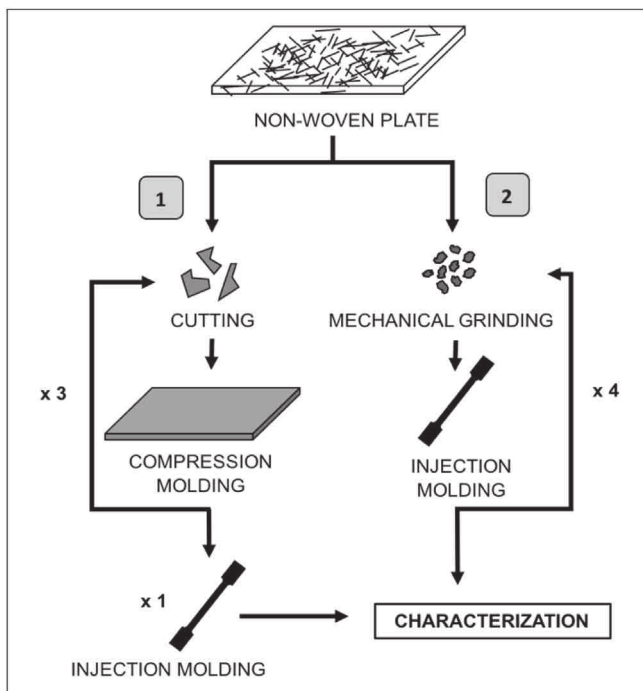


Fig. 1. Valorization routes for non-woven plates.

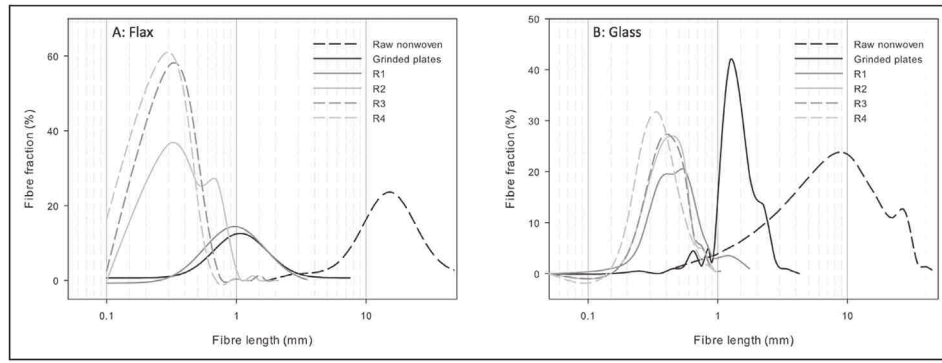


Fig. 2. Distribution of flax (A) and glass (B) fibre length before and during recycling.

2.7. Rheological experiments

To investigate the effect of recycling on the rheological properties of the recycled materials and check the consistency with standard injected materials tests such as viscosity measurements of the melt materials were performed. The granulated composites were dried at 60 °C for a period of 15 h prior to testing. The tests were carried out on initial shredded plates and after each injection cycles (including the last injection following the compression moulding recycling cycles). A capillary rheometer (Göttfert RG20, Göttfert, Buchen, Germany) was used to measure the shear viscosity of the melt. The barrel temperature was pre-set to 190 °C. The samples were heated for 300s in the barrel and then extruded through 10, 20 and 30 mm length and 1 mm diameter dies. The experiments were performed at increasing shear rates of 10, 50, 100, 500, 1000, 2000, 5000 and 10,000 s⁻¹. The pressure needed to extrude the material through the 3 dies at each shear rate was recorded when constant (less than 3% deviation) reading values were reached. After the experiments, the Bagley [43] and Rabinowitsch [44] correction were applied to correct the apparent shear rate and to calculate the true shear viscosity.

3. Results and discussions

3.1. Recycling of non wovens composites by successive injection moulding cycles

3.1.1. Evolution of fibre morphology along the cycles

Fig. 2 shows the distribution of flax (3. A) and glass (3. B) fibre length before and during recycling. Initial fibres extracted from raw non wovens, and particularly glass ones, exhibit a large distribution indicating heterogeneous fibre morphology. For glass fibres, we can observe the presence of two populations (around 9 and 38 mm) probably due to the fibre cutting tool. Whatever for flax and glass fibres, mechanical grinding induces a drastic drop of length but also a narrower distribution. The first injection cycle has also a strong impact on the glass fibre length, the average fibre length in granulates and injected materials being 1.46 ± 0.58 mm and 0.54 ± 0.19 mm, respectively. This represents an important drop (-63.0%) in comparison to the decrease in flax fibre length for the same processing steps (-24.7%). This difference can be attributed to the important apparent stiffness of glass fibres, inducing an easier breakage of these elements compared to the flax ones. This significant decrease of length after processing is generally observed in other studies on flax fibres [45,46] but also on glass [23] as injection steps are aggressive with important mechanical and thermal solicitations. Until R1 and R2 cycles, for glass and flax, respectively, one can notice that two populations of length remain visible; after

R2, the fibre length continues to regularly decrease but the important cumulated shear rates supported by the fibres induce an improvement of the length scattering. Moreover, we can notice that the fibre length does not show important evolutions for the last cycles. This means that the shear rate has no effect on the fibre length when the fibre exhibit low values of length. This phenomenon was highlighted by different authors [11,46,47]. Regarding fibre length, we might consider that flax and glass exhibit quite similar behaviours all along the process cycles.

The evolution of fibres aspect ratio (L/D) is showed in Table 1. The fibre aspect ratio is a key parameter that directly influences the stress transfer ability [48]. A fibre aspect ratio superior to 10 is considered to be the minimum value for good stress transmission. In our case, the average aspect ratio after the injection moulding cycle for flax and glass is 54.2 ± 29.8 and 35.3 ± 7.2 , respectively and this value remains always over 20, even after four recycling cycles. For glass fibre composite, one can notice that the fibre aspect ratio always decreases due to the presence of single fibres all along the process cycles. Consequently, this parameter is controlled by the length evolution. Interestingly, this tendency is different for flax fibres as non-wovens are mainly constituted of flax scutched tows [33,42] that are constituted of more cohesive bundles in comparison to long well scutched and hackled fibres. The first injection cycle strongly divides these fibre bundles and consequently, a significant increase into the fibre aspect ratio is then noticed, length being moderately affected as described previously.

Table 1

Evolution of the fibre geometry before and during the injection moulding recycling for PP/flax and PP/glass composites

PP/flax			
Step	Aspect ratio (L/D)	Length (mm)	Diameter (μm)
Raw non-woven	232.3 ± 42.4	19.51 ± 7.12	89 ± 33
Granulated material	40.8 ± 26.9	1.74 ± 1.16	50 ± 30
First recycling (R1)	54.2 ± 29.8	1.31 ± 0.61	27 ± 9
Second recycling (R2)	30.2 ± 18.0	0.53 ± 0.22	20 ± 6
Third recycling (R3)	22.9 ± 13.7	0.39 ± 0.16	19 ± 5
Fourth recycling (R4)	20.3 ± 10.3	0.29 ± 0.11	17 ± 6
PP/glass			
Step	Aspect ratio (L/D)	Length (mm)	Diameter (μm)
Raw non-woven	923.8 ± 52.8	15.73 ± 9.01	18 ± 4
Granulated material	83.2 ± 11.1	1.46 ± 0.58	18 ± 4
First recycling (R1)	35.3 ± 7.2	0.54 ± 0.19	18 ± 4
Second recycling (R2)	31.7 ± 5.1	0.47 ± 0.17	18 ± 4
Third recycling (R3)	26.2 ± 4.8	0.46 ± 0.13	18 ± 4
Fourth recycling (R4)	23.1 ± 5.2	0.41 ± 0.14	18 ± 4

3.1.2. Composites rheological behaviour

Fig. 3 shows the evolution of the apparent shear viscosity as a function of the apparent shear rate for flax (A) and glass (B) granulated materials and injected composites. These curves were obtained by capillary rheology experiments. During processing, fibres move and rotate with the flow of the polymer matrix, which inevitably changes their orientation state and could affect the properties of composite materials [49]. Moreover, flow properties could depend on fibre length, stiffness, strength, volume fraction and nature of fibre matrix adhesion [50]. Composites studied in our paper are made with the same polymer. Therefore, the main parameters which can differ and act on the molten materials properties are fibres orientation and length.

The results of capillary rheology tests show the shear rate dependency of composites. It is noteworthy to mention that the flax material shear dependency is different to the one of glass composites. The flax composites are more shear dependent than the glass ones. Ryszardet et al. already reported that the viscosity of the composite system is more non-Newtonian, i.e., its viscosity is more dependent on the shear rate in comparison to the virgin polymer [51]. This phenomenon is highly pronounced for flax materials, particularly for low shear rates. This result is coherent with the ones of Gamon et al. [52] and Kalaprasad et al. [50]. At lower shear rates, the fibres are disoriented and polymer chain entangled as the shear rate is insufficient to ensure the mobility of the system. As a consequence, the viscosity increases. Regarding flax composites, due to the important diameter and length of flax bundles until R2 cycle, one can assume that a low shear rate is not able to correctly individualise the fibre elements. In composite fibre blends, the aspect ratio is considered to be the most influent parameter for the viscosity increase [53]. In our case one can notice that rheological behaviour is different, (for flax and glass), when the aspect ratio value is over 40 (Table 1). Thus, for low individualised bundles, curves exhibit a more pronounced non-Newtonian behaviour. When L/D decreases, composite becomes more homogenous and the shear rate dependency is less important, especially when glass is used. Indeed, glass fibres are highly individualised and facilitate the polymer flow. Consequently, on a general way, viscosity of PP-glass and flax non-woven are very different. As an example for a shear rate of 500 s^{-1} , the viscosities of PP/glass and PP/flax are 230 Pa s and 650 Pa s , respectively.

Regarding the intrinsic values of viscosity, an evident decrease in apparent viscosity as a function of the number of recycling cycles (Fig. 3A and B) is observed. For 500 s^{-1} , this viscosity drop is -64.7% and -73.3% , for the flax and glass composites respectively. As explained previously, for the first cycle, a high composite viscosity value is observed due to the presence of long fibres which cause a restriction of the chain mobility of the matrix due to the

fibre–polymer and fibre–fibre interactions. During recycling, the viscosity significantly decreases confirming a strong reduction of the fibre length and diameter. Several authors have described the influence of the fibre length on the viscosity of thermoplastic composites [23,54].

In this work, we used a PP matrix which is not very sensitive to shear rate [23] and which viscosity does not change very much as a function of the successive recycling cycles. The observed decrease in viscosity is thus mainly due to the evolution of the morphology of the fibres and cannot be considered as a problem.; On the contrary, it can be viewed as an advantage to ease the flow in the injection or extrusion tools.

3.1.3. Microstructural analysis of recycled composites

Two specific routes were explored to investigate the composites microstructure. SEM observations were performed in a first extent. Fig. 5 shows SEM cross sections images of flax and glass composites after 1 and 4 injection cycles.

In the case of flax composites, SEM images confirm the results observed on fibre length measurements; the strong decrease in length between the first and the fourth injection cycles (-83.3%) can be estimated from SEM images. The same applies to diameters. In Fig. 4A, numerous bundles of fibres are present, which makes the material very homogeneous. As described in a previous work [33], non woven PP-flax materials are constituted of few elementary fibres but also of fibre bundles and shives which are clearly visible on Fig. 4A. After four cycles, even if a few fibre bundles remain, they exhibit much smaller dimensions. Their mean diameter is reduced by 37.0% . After four cycles, the observations revealed a much stronger skin-core effect. The specimens display a layer of skin of a few hundred microns with a majority of fibres aligned in the direction of the flow whereas in the core this orientation does not exist as the fibres are oriented more randomly. This phenomenon has already been demonstrated by different authors both on injected composites reinforced with synthetic or plant fibres. Apart from this more pronounced skin core effect, one can note a much greater homogeneity of the material after four cycles of injection. For the PP-glass non-woven samples, no bundle is visible, the fibres being perfectly individualised at the beginning of the process. However, as with flax, the material is more homogeneous after four cycles. Due to the lower fibre length the differences in microstructure are, however, less marked than for flax fibres, characterised by very dispersed diameters in the first cycle. For both the first or fourth cycles, the skin's core effect is clearly visible. Fibres transversally oriented to the flux are visible in the middle of the specimen for both the first or fourth cycle. However, this skin-core effect is much more accentuated at the fourth cycle as the core part is highly reduced and most of fibres are oriented in the flow direction.

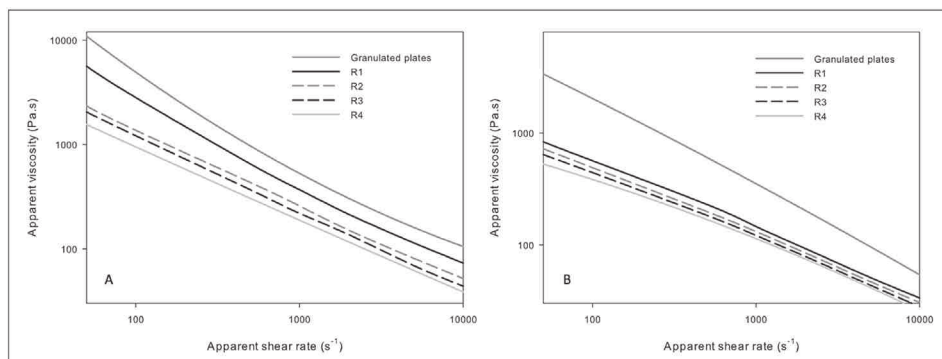


Fig. 3. Apparent shear viscosity versus apparent shear rate for flax (A) and glass (B) granulated materials and injected composites.

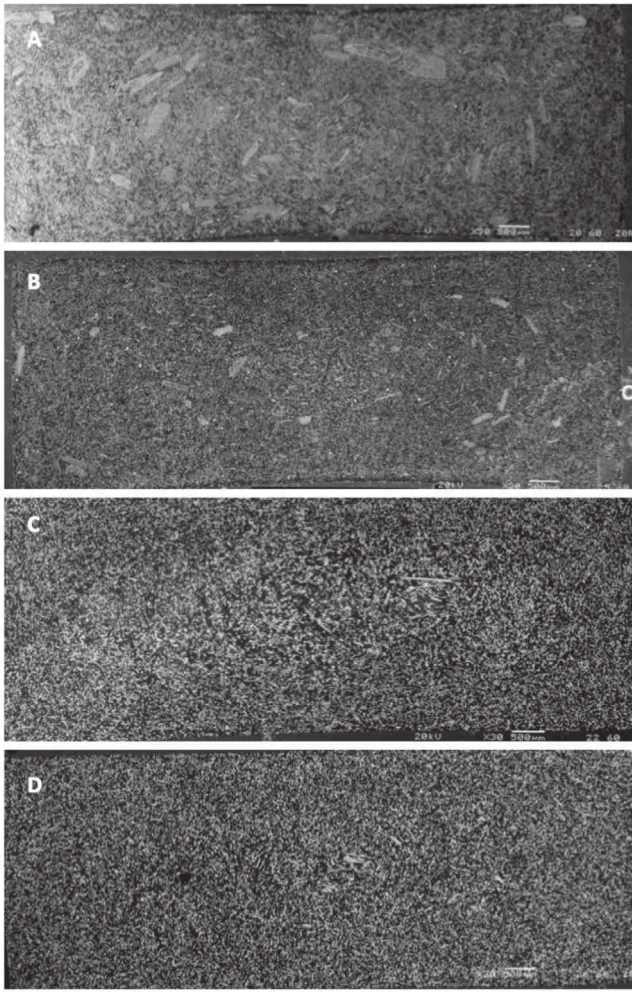


Fig. 4. SEM cross section observations of recycled injected composites: PP/flax at first (A) and fourth cycle (B); PP/glass at first (C) and fourth cycle (D).

Tomographic analysis was performed to investigate the evolution of the porosity rates after each recycling cycles. Fig. 5 shows the evolution of porosity in injected samples cross sections. Interestingly, and as discussed previously, the tomographic results confirm the improvement of the samples' homogeneity with the recycling, especially for flax composites. For glass materials, due to the good fibre individualisation the porosity rate is very low whatever the considered cycle. For flax composites, localised area between 1 and 2% of porosity can be noticed in the middle of the specimen where the heterogeneity is the highest. These porosity contents are consistent with published data on similar materials and also investigated by tomographic method [31]. After 4 injection cycles, the porosity is not observed anymore. It is almost not present anymore for both glass and flax/PP materials. The results given in Fig. 5 highlight the fact that low levels of porosity are measured for all the investigated samples. This demonstrates that the level of porosity is not influenced by the recycling cycles. This is probably due to the high pressure used during the injection process, especially compared to porosity levels of thermoset composites.

3.1.4. Composites mechanical properties

Fig. 6 shows the mechanical tensile performances of both the initial flax (Fig. 6A) or glass (Fig. 6B) non-woven samples and the injected composites. The mechanical performance of the PP matrix is also indicated.

One can notice the good mechanical performance of the flax plates with a Young modulus and a stress at break equal to 8.7 ± 0.9 Gpa and 42.5 ± 2.5 MPa, respectively. These data are in the same range than previous values obtained on PP-flax non-wovens [42] and, for the same fibre volume fraction, outperform injected composites [55] due to the important length of flax fibres within the material. Of course, this important stiffness is counterbalanced by the very low value of strain at break ($1.1 \pm 0.1\%$), especially due to the important fibre loading. After grinding and injection, a significant drop of the mechanical properties is noticed. Young's modulus and strength at break are reduced by 35.6% and 48.2% respectively after the first injection cycle. This decrease is clearly induced by the drastic decrease of the fibre length but also by the use of non modified PP; literature strength at break are generally higher in case of use of maleic anhydrid PP. Interestingly, after the first cycle, the modulus and strength values globally remain stable; even if the length of the fibres continues to decrease (Table 1) for successive cycles. The aspect ratio is poorly impacted and, as evidenced on SEM images, the homogeneity of the composite structure is clearly better after 4 injection cycles (Fig. 4B).

The same tendencies can be observed for glass non-wovens. One can notice very interesting mechanical performances of the initial composite plates, especially for modulus with a value of 11.2 ± 0.9 GPa, compared to literature [18,19,21]. The injection moulding process modifies the composite structure and leads to a drop of 8.0% and 60.5% of the Young modulus and strength at break, respectively. The most pronounced fibre orientation in the flow direction, compared to flax composite, is in favour of high modulus. However, the important fibre length drop (-63.0%) after one injection cycle strongly affects the strength at break. Modulus and strength at break are decreased with low extents for successive injection cycles with evolutions of -8.3% and -6.7% , respectively, between the first and the fourth cycle. This evolution can be attributed to the length but also to the PP-fibre interface modification due to the loss of efficiency of fibre sizing, as demonstrated previously [23].

3.2. Study of an alternative recycling route: compression moulding

As mentioned in the introduction part of this paper, a new innovative recycling route using cut pieces of composite materials is explored. After manufacturing an initial composite plate using non-woven comingled mats, three successive recycling cycles were performed by using compression moulding of randomly arranges square grains that cover 75% of the mould surface. Finally, a fourth recycling cycle was performed using the injection process to investigate if the material can still be recycled for a last series of application.

3.2.1. Evolution of the fibre length

Fig. 7 shows the evolution, for flax and glass compressed plates, of the fibre length for initial non-woven composites but also after three compression moulding recycling cycles. In addition, the fibre length of injected specimens, after the last recycling cycle (R4) of both injection and compression moulding are showed. As expected, a lower decrease in the fibre length can be noticed after 3 cycles of compression moulding compared to injection recycling (Table 1); indeed, the residual length of flax and glass are 4.22 ± 1.12 mm and 3.04 ± 1.85 mm, respectively. The fibre length reduction in both cases is of about a factor 5. Fibre length of 0.39 ± 0.16 mm and 0.47 ± 0.17 mm, respectively for the same step after recycling by injection are observed. The fibre length after three injection steps is reduced by a factor 50 for flax/PP whereas it is only reduced by a factor 34 for glass/pp. The fibre length after three compression moulding recycling cycles are therefore more than 10 times higher

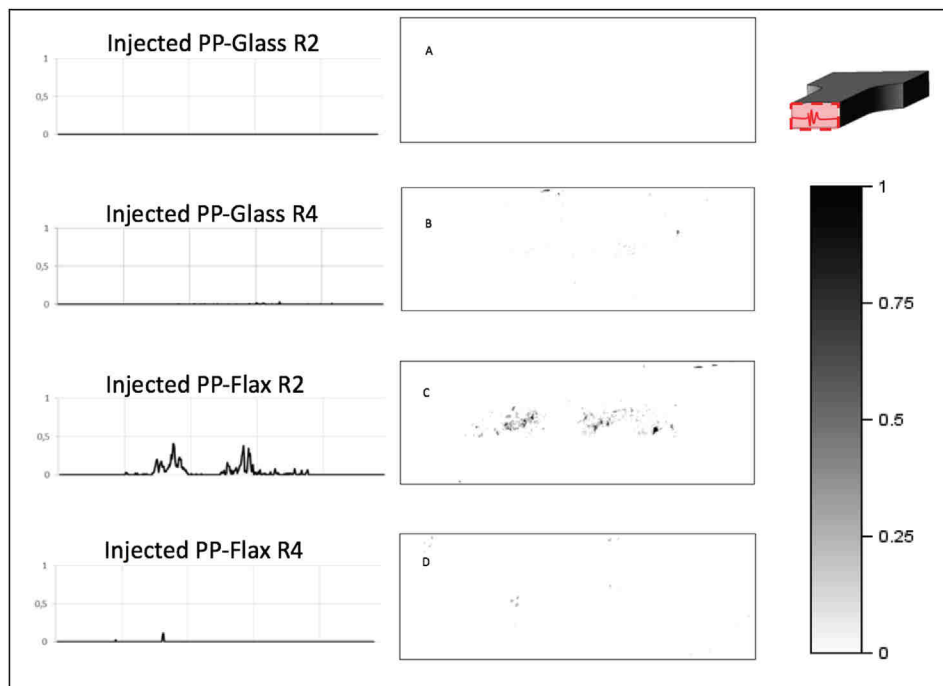


Fig. 5. Evolution of porosity content through tomographic analysis: injected PP/glass at second (A) and fourth cycle (B); injected PP/flax at second (C) and fourth cycle (D); profiles of porosity rate in the middle of injected samples are added.

than the one encountered after three injection recycling cycles. This important difference is mainly due to the important shear rate induced by the extrusion and injection processes. For compression moulding, shear rate is generally of about 5 s^{-1} [56] whereas it is more than $10,000 \text{ s}^{-1}$ [57] for injection moulding. After a fourth cycle by injection moulding that follows three compression recycling cycles, for both flax and glass fibres, the final length is 0.8 mm which is significantly higher than for a fully injection recycling process (0.29 for flax and 0.41 for glass). The flax and glass fibres after a fourth injection cycle after three compression recycling cycles are therefore more than twice longer than in the case of a fourth cascading injection cycle. This conservation of significant fibre lengths is in favour of better mechanical performances.

3.2.2. Tomographic analysis

Additional informations are given by tomographic investigations. Fig. 8 compares the microstructure of a glass and a flax plate after one and three compression moulding cycles. After one cycle, the fibre network is not homogenous and some limits and boundaries between initial square pieces of cut composites are visible. Moreover, due to the limited shear rate, one can notice the presence of resin rich areas. After three cycles, the part microstructure is significantly more homogeneous in spite of remaining heterogeneities in the fibres dispersion, probably inducing variation into the local fibre volume fraction. Interestingly, the fibre length does not seem to be very much impacted by compression recycling (at least between R1 and R3). One can therefore suppose that the decrease in the fibre length is mainly caused by the first recycling.

Analysis of the microstructure of injected samples after injection or compression moulding has also been performed. Fig. 9 shows the differences in local fibre volume fraction in injected samples (R4) after both compression or injection moulding for the three first cycles. For each sample, a cartography of the local fibre volume fraction in the middle of the sample (averaged from 10 measurements) is showed as well as a profile along the sample

width, from a mould wall to another. Significant differences can be noticed according to the recycling way. In case of fully injection recycling, moderate skin-core effect is noticed, for glass and even more for flax composites. These observations are in line with conclusions obtained from SEM images (Fig. 4). After a compression recycling, things are strongly different; the skin-core effect is much more pronounced with fibre volume fraction significantly higher in the core area for flax composites but also for glass ones. This phenomenon is clearly induced by the difference in fibre length, which leads to an increase of the melt viscosity and consequently a decrease in the filling speed and an increase of the core thickness. The samples morphology is also highlighted in Fig. 10 where fibre orientation along the flow is evidenced. Due to more pronounced density difference between PP matrix and glass fibres, compared to flax and PP, orientation and length of glass fibres are visible. Thus after compression recycling cycles, samples morphology and microstructure of injected samples are fully changed if one compares to the microstructure of a fully injected sample. Skin-core effect is more pronounced, r for both glass and flax. Fibres are not only longer but also more oriented in the flow direction.

3.2.3. Mechanical assesment

Fig. 11 shows the evolution of the tensile strength and Young's modulus after three compression moulding recycling steps and one final recycling cycle using injection moulding. In Fig. 11, one can observe that the tensile properties of the studied PP are well reinforced by the random fibres for both flax and glass based materials. One can also observe that the glass fibre reinforced PP show higher properties than the ones reinforced by flax fibres. The strength and modulus of glass reinforced PP are about 1.3 times higher than the ones of flax/PP composites. This is not really surprising and this is probably due to the fact that the access to the reinforcement fibres is higher in glass than in flax. Indeed, the individualisation of flax fibre is relatively low in the random flax mat, and some individual fibres within bundles are not accessible to the resin and therefore do not directly reinforce the composite

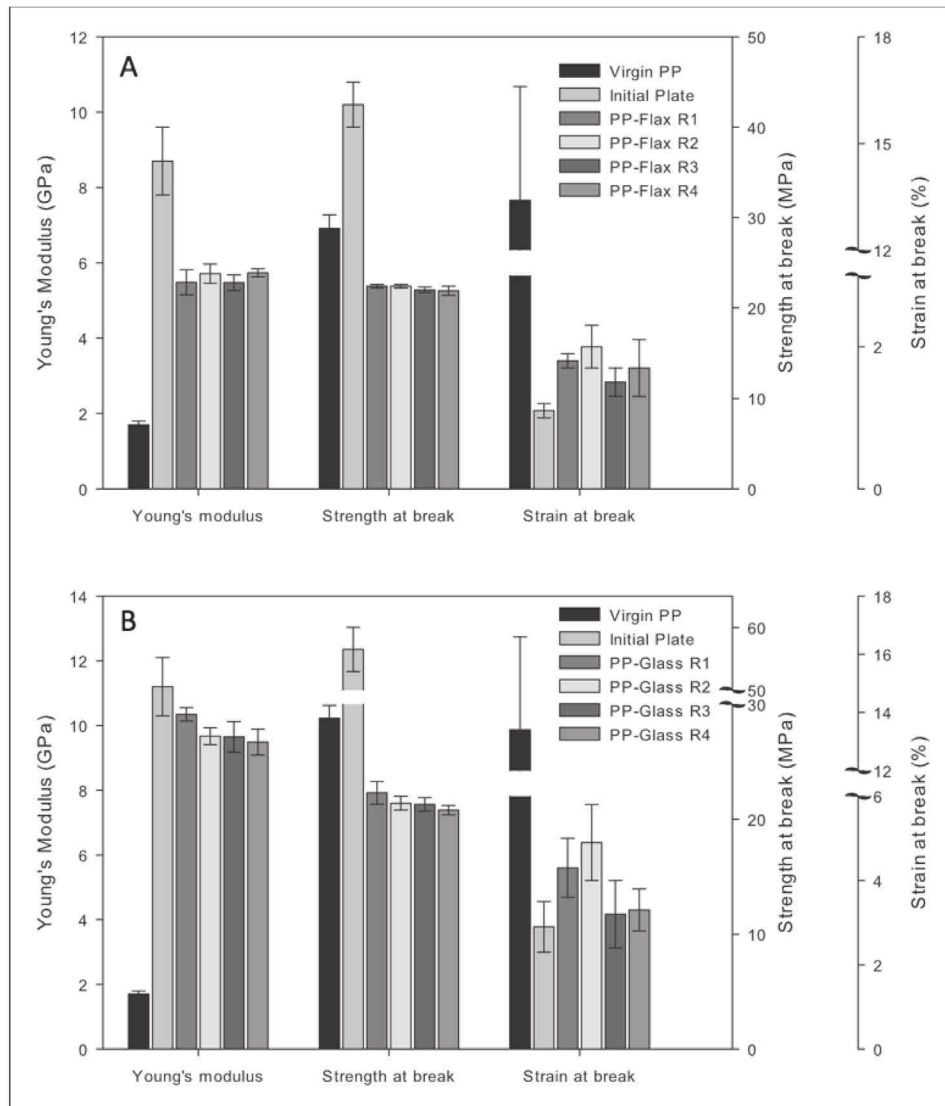


Fig. 6. Evolution of tensile modulus, strength and strain at break for PP/flax (A) and PP/glass (B) recycled composites.

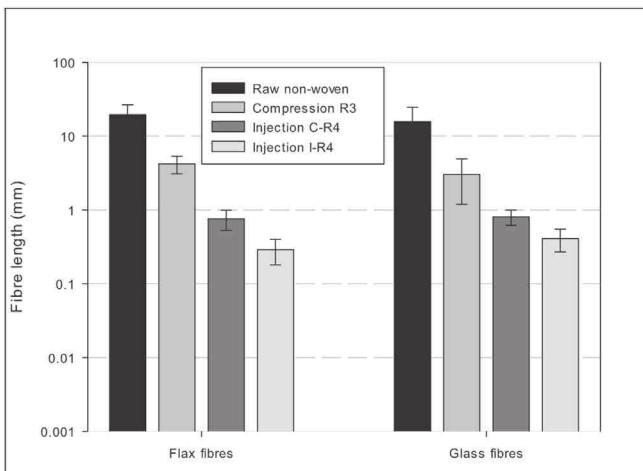


Fig. 7. Evolution of fibre length after compression moulding; values of 4th injection cycle (after injection (I-R4) or compression (C-R4) recycling) are also indicated.

material. Moreover, as highlighted in a previous work [45], the fibre interfaces within bundles were identified as zones of weakness and preferential crack initiation areas. The use of more individual flax fibres should favour an increase in tensile strength and modulus.

After a first recycling cycle, one can observe that the tensile strengths of the flax and glass reinforced PP decrease respectively by 70 and 75% compared to raw non-woven materials. This is mainly due to the fact that resin rich zones that are identified as zone of weakness can be identified and easily visualised on Fig. 8a and b for glass and flax, respectively after a first recycling cycle. Some of the resin rich zones are also situated between two square particle edges. Stress concentration may be expected to take place in those zones. The important decrease in fibre length (even if the fibre length is 10 times higher than for injection moulding (Fig. 7) can also play a role in this drop by penalising the stress transfer between fibre and polymer matrix but also by encouraging the debonding of the fibre from the polymer.

After a large decrease in tensile properties observed during the first recycling cycle, only low decreases are observed in the two following cycles. Despite the presence of remaining zones of weakness in the microstructure of the R3 plate for example (Fig. 8C

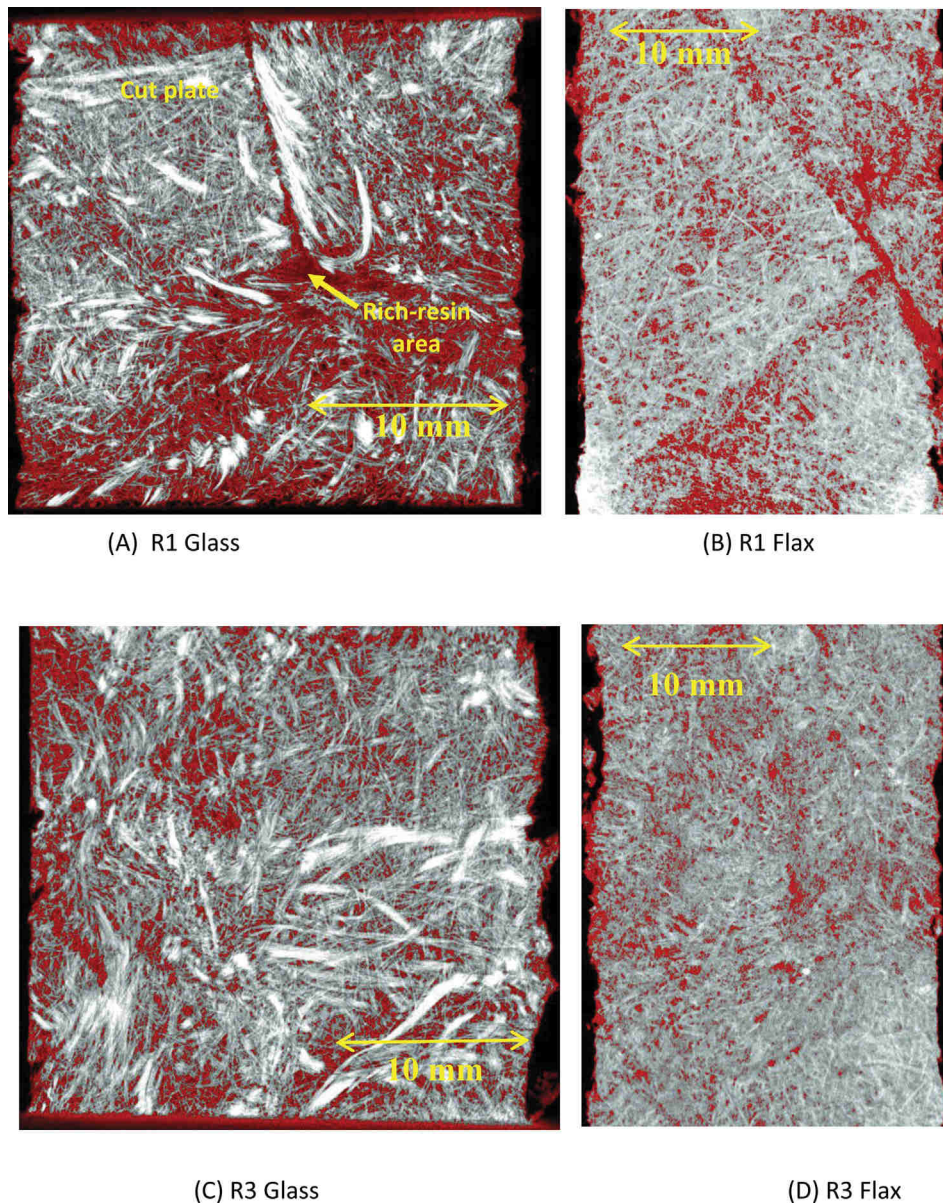


Fig. 8. Tomographic analysis: Views of glass and flax/PP parts after a first (A and B) and a third cycle (C and D) recycling cycle by compression moulding. The zones in white and grey are representative of the resin and the zones in red are representative of the resin. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and D), one can notice that the sizes of the resin rich zones are globally lower than for R1. Moreover, Fig. 8 suggests that the dispersion of the fibres is more homogeneous after the third recycling cycle R3. As an example the square cut particles are not really visible anymore. The zones where stress concentration was suspected to take place are not observed anymore. For the modulus, the decrease observed after the first recycling cycle is not as strong as the one observed for strength. Decreases of 30% of the modulus is observed after the first recycling of the flax/PP composite. In the case of glass/PP the decrease in modulus is of about 3% but is not significantly different than the one of the initial composite. The decrease in modulus can be attributed generally to a reduction of the fibre length, to the amount of porosity of a material or to degradation of fibre/resin interface for example. In our case, the amount of porosity was estimated from an analysis on different volumes of the part in the same manner as for the injected parts

(Fig. 5). Porosity measurements performed on different volumes of the parts indicate that the level of porosity remains constant for the different recycling cycles (less than 1% for both flax and glass after R1 and R3). One could suppose that in this case, the reduction of the modulus may be due to the reduction in fibre length as shown by Fig. 7. However, the length of the fibres after cycle 3 are globally equivalent (Fig. 7). One could hypothesise that the reduction in flax fibre length is more severe than in the case of glass because of their arrangement in bundles. This may be attributed to the fact that the fibres in the glass mat are more separated and therefore cutting the composite into square pieces does not affect the fibre length with the same extent. Other reductions of modulus are also observed for flax for the second and third recycling cycles. Once again, the reduction in modulus is attributed to the reduction of the flax technical fibre length. It may also be due to reductions of the fibre/matrix interface quality. For the glass second and third recycling

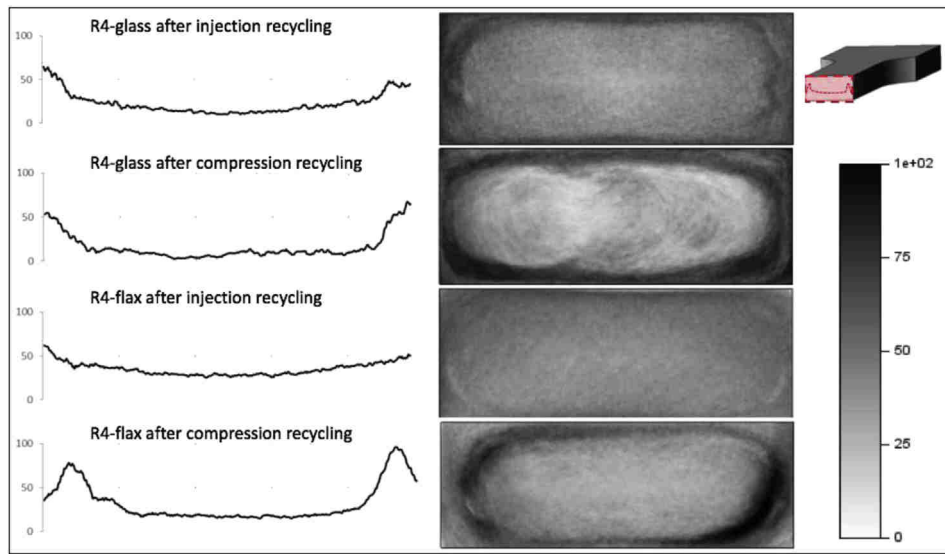


Fig. 9. Tomographic analysis of local fibre volume fraction after injection moulding.

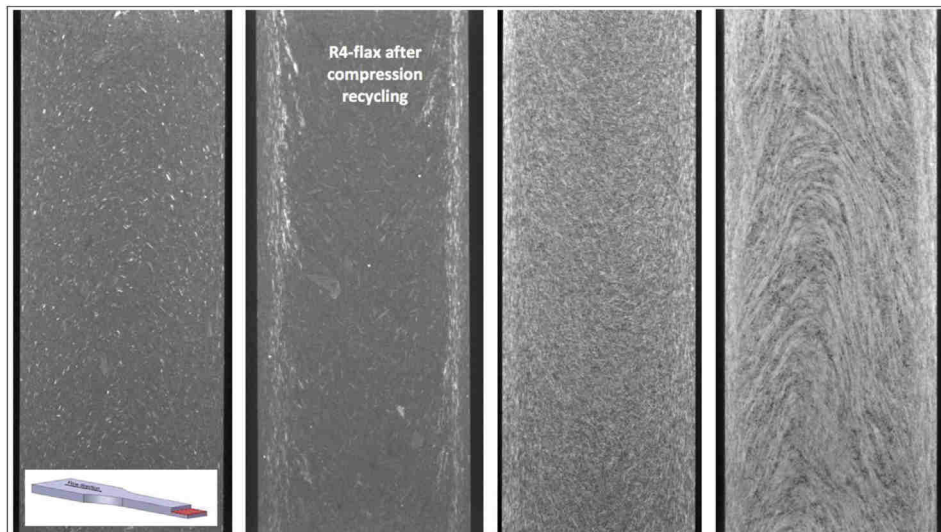


Fig. 10. Tomographic analysis of fibre orientation after injection moulding.

cycles, the modulus does not change significantly. This behaviour can be explained by the fact that the reduction of the fibre length is compensated by a better arrangement of the particles in the material, with less discontinuities.

Fig. 11 shows that the tensile properties, strength and modulus, increase with a great extent after the fourth recycling by injection moulding. For flax, the strength and modulus are respectively increased by 103% and 75%. For the glass/PP fourth recycling cycle, the strength and modulus are increased by 133% and 42%. Fig. 9 shows that the injection moulding process after recycling cycles by compression moulding has for consequence to favour a core skin effect. The concentration of fibres at the periphery is much higher than in the core of the sample and the alignment more pronounced in the flow direction which is also the loading one. The percentage of fibres in the peripheries of the sample can be higher by a factor 3 for flax and by a factor 10 for glass. Besides, the very large shear that take place at the periphery of the sample has for consequence to align the fibres. This therefore explains why the modulus is greatly

increased. One may also suppose that the level of alignment is more important for flax than for glass. This may be due to the fact that the fibre bundles are more rigid and therefore align themselves more easily with the flow. For the strength, the rise of property for both flax and glass may be explained by the decrease of defects. Even if the fibre concentration is not uniform, (Fig. 9), no defect such as resin rich regions with stress concentration zones can be observed with the apparatus used in this work. More applied stress therefore needs to be applied to initiate a crack.

3.3. Overall discussion and assessment

A number of comments can be added in the continuity of these scientific results concerning the recycling of non-woven hybrid PP-flax or PP-glass composites. The two routes explored, recycling by injection or by compression, have their limits and their advantages.

In terms of morphology of the parts, the behaviours are radically different between the two processes. Compression moulding

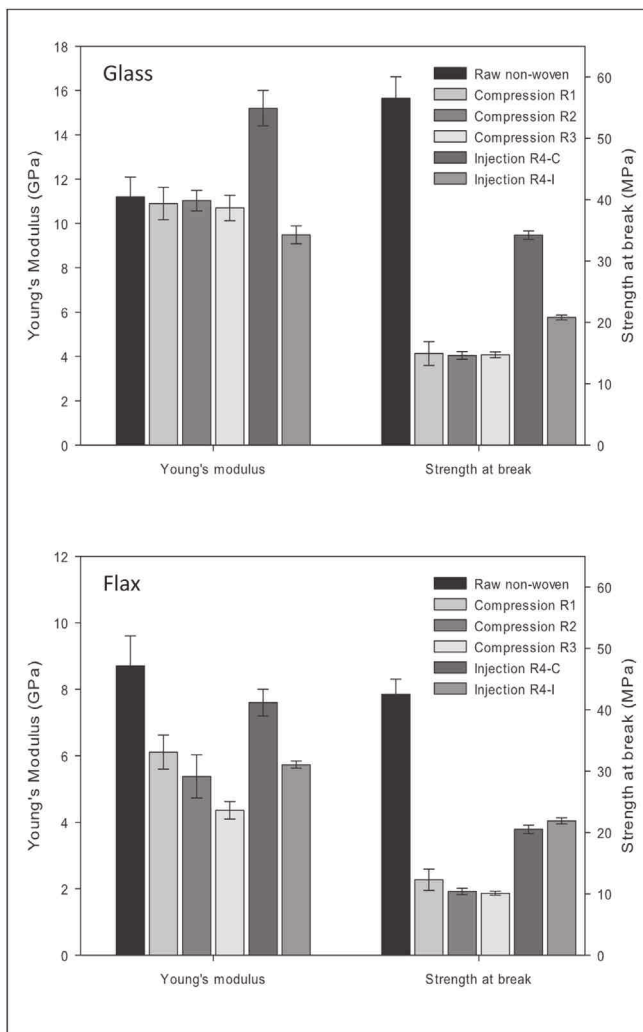


Fig. 11. Tensile Young's modulus and strength at break of composite after compression recycling. Values after injection are added for cycle 4 after compression (R4-C) or injection (R4-I) recycling process.

provides long-lasting fibre lengths and has a lower impact on the geometries of these fibres. On the other hand, by its nature it favours the presence of resin-rich zones located in the inter-particle joint zones. This mode of recycling also has for consequence to maintain the isotropic nature of the non-woven parts by not promoting any direction for the orientation of the fibres. Injection moulding, because of the high shear rates it generates, causes a drastic drop in the length of the fibres, but this is counterbalanced by a strong orientation of the fibres in the direction of flow. It also induces an important skin-core effect that tends to become more marked with recycling cycles. Major differences in terms of fibre volume levels also appear in the injected test pieces. These points, related to the flow of the material in the tools, should be put into perspective because they are strongly dependent on the geometry of the parts. The long test pieces injected at the end of the specimen naturally favour a privileged orientation in the length of the parts which is also the direction of the mechanical stresses in tensile mode. We can imagine that in the case of a large and thicker part or with multiple injection points, the microstructure would be radically different. For large parts and after recycling, compression is likely to have a significant advantage as it guarantees isotropic and better mechanical performance due to fibre length. To conclude on the morphological characteristics, we could show that the injected

parts have very low porosity levels, combined with high fibre content, because of the high pressures involved. Moreover, the injection offers the possibility to homogenise the microstructures because of the substantial shear rate which occurs during this process.

In terms of the mechanical behaviour of the composite structures, the two modes of manufacture and recycling also have advantages. Compression moulding has for effect to better preserve the initial length of the fibres and in this way promotes the stiffness of the parts. Injection moulding has the advantage of dividing and strongly individualising the fibrous elements which is favourable to a mechanical stress of quality. In the case of compression moulding, the stress level is strongly limited by the resin-enriched areas which constitute areas of weakness and preferential damage within the composite. Depending on the preferred final characteristics, one or the other of the recycling modes may be chosen.

In addition to these technical considerations, the choice of the recycling technology is also conditioned by economic criteria. Injection is reserved for large volumes while compression moulding can be used for small series. The nature and the volume of the available deposits can guide this choice. One could imagine that recycling by compression is more suitable in the case of modest deposits, for which the recycling is done locally or in the form of short circuit. These devices are easily adaptable at producers of non-woven composite parts that already have thermal-compression machines., Injection recycling, which requires large volumes could be used more globally and to gather waste from different horizons.

4. Conclusion

The work presented in this paper investigated the possibility to perform multiple recycling of non-woven based composites by a traditional injection moulding technique and by a more novel compression moulding procedure. The impact of the two recycling routes was also investigated on the microstructure of the fibres and on the tensile properties of the new generated material after each recycling cycle. The results presented in this work showed that the compression moulding permits to keep fibres length about 10 times larger than for the injection moulding process and therefore prevent a too important decrease of the modulus. After three compression moulding recycling cycles, the decrease in modulus is of about 40% for flax/PP and only 4% for glass/PP composites. However, due to inherent defects such as resin rich regions the tensile strength of compression moulding flax and glass/PP show 70 and 75% decreases. If injection moulding has for consequence to reduce the fibre length to values lower than 1 mm, it also promotes good fibre dispersion, high fibre volume fractions and almost defect free microstructures. This has for consequence to promote high strength materials. In the frame of recycling, the decrease in strength after the first cycle is of about 50%, but does not evolve anymore for the successive cycles. One could therefore opt for the compression moulding recycling process in the case of part that needs to be designed for its rigidity and for the injection moulding in the case the strength is the main design criterion. The compression moulding process can be used with a relatively simple equipment that is often available in composite manufacturing facilities. Small series can be considered on the contrary to injection moulding that requires larger investments and higher amounts of material to recycle.

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