MECHANICAL RECYCLING OF FLAX, BASALT AND HYBRID POLYPROPYLENE COMPOSITES

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ABSTRACT

Hybridization of vegetable fibres with basalt ones is widely exploited to simultaneously take advantage of vegetable fibres environmental benefits and basalt fibres improved mechanical properties. Despite the progressive spread of this composite solution, no study assessed the mechanical reprocessing of this type of materials. Therefore, the present work aimed to investigate the effects of mechanical reprocessing on the microstructure, the thermal and mechanical behaviour of flax/basalt hybrid polypropylene composites up to seven reprocessing cycles. A comparison with basalt and flax composites was also provided to disclose the effects resulting from the interaction of flax and basalt fibres in the hybrid configuration. It was found out that this interaction is responsible for a faster decrease in flax fibres length thus causing a strong decrease in hybrid mechanical performance already at the second reprocessing cycle. Despite this, hybrid composites remain competitive displaying a higher flexural stiffness and strength and an improved impact strength at -50 °C, room temperature and +50 °C at the second reprocessing cycle compared to flax composites while basalt composites remain competitive up to the third reprocessing cycle. In light of the easier processability of hybrids and basalt composites resulting from the higher MVR, their mechanical recycling can be conveniently exploited to produce components traditionally manufactured with flax fibres.

1 INTRODUCTION

Waste generation and the related management are big challenges that need to be faced to meet the new regulation encompassed in the European 2008/1/EC directive in the field of Integrated Pollution Prevention and Control (IPPC). Particular attention is paid to plastic wastes which represent almost 12 % of total wastes [1] and only a small part is properly recycled, i.e., 33 million tons of the 353 produced in 2019 [2]. In this perspective, great efforts are requested to industrial fields such as packaging and transportations to promote greener policies oriented to materials reuse and recycling considering their massive use of plastic components, i.e., 31 % and 12 %, respectively [2].

Focusing on the automotive sector which has to face the restrictions imposed by the new vehicles end-of-life regulations (2000/53/EC), a special attention must be drawn on polypropylene (PP) which is the main thermoplastic polymer employed, accounting for over the 16 % in both polymeric and composite components.

Considering that glass fibres account for more than 95 % of the total amount of reinforcements used at an industrial scale [3], glass fibre reinforced PP composites were the first ones to be investigated in a circular economy perspective of material recycling [4,5]. In all cases, a strong decrease in composite mechanical performance was observed due to fibre length reduction with a drop of 50 % and 45 % in tensile strength and flexural modulus after 10 reprocessing cycles, respectively [5].

Further studies focused on the mechanical recycling of eco-friendlier PP composites produced with vegetable fibres, e.g., wood [6,7], flax [5,8], kenaf [9], considering their progressive market entry for non-structural components manufacturing. Their exploitation in door panels, package shelves, trays, etc. [10] to produce automotive parts characterized by a lower carbon footprint [11], made necessary the identification of suitable recycling paths.

To increase the product range where vegetable fibres could be used considering the lower mechanical output resulting from their composite, hybridization with more mechanical performing ones such as glass, was largely investigated to exploit vegetable fibres environmental advantages while preserving composites mechanical properties. Further environmental benefits were achieved as a consequence of basalt fibres appearance on the market, which ensures mechanical properties comparable with E-glass ones and a greener manufacturing process [12].

Despite the many studies which proved the potential and the advantages of hybrids [13], no studies are available on the mechanical reprocessing of hybrid basalt/vegetable fibres composites and the effect arising from the interaction of different fibres on composite mechanical performance and microstructure was never disclosed before.

Mechanical reprocessing of flax/basalt hybrid PP composites was assessed in the present work and the changes in morphological, thermal and mechanical properties were investigated up to 7 reprocessing cycles. A comparison with PP reinforced with only flax and only basalt fibres was also provided. Fibre length distribution, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), Melt Volume Flow Rate (MVR), tensile tests, 3-point bending tests and Charpy impact tests are the characterization techniques used to provide a comprehensive overview of the effect of mechanical reprocessing on this class of composite materials.

2 MATERIALS AND METHODS

2.1 Materials and composite manufacturing

All PP composites were produced by coupling extrusion with injection moulding. The PP matrix used was the Isplen PP094 by Repsol while the short basalt (diameter of 13 μm and nominal length of 6.4 mm) and flax (nominal length of 2 mm) fibres were supplied by Incotelogy GmbH and Teillage Vandecandelaere, respectively. The PP matrix was modified with a 5 wt.% of maleic anhydride grafted polypropylene (MAPP) Polybond 3200 supplied by Addivant Corporation to increase the compatibility with the fibres. Table 1 summarizes the five configurations under consideration.

Configuration	PP	MAPP	Flax	Basalt
PP	100	-	-	-
MAPP	95	5	-	-
Flax	65	5	30	-
Basalt	65	5	-	30
Hybrid	65	5	15	15

Table 1: All composite formulations produced and tested in the present study (wt. %)

A co-rotating twin screw extruder, Thermo Scientific Process 11, with a temperature profile of 185–190–200–210–210–200–200–200 °C and a screw speed of 150 rpm was used to compound the raw materials. The compound was injection moulded with a Haake MiniJet II Pro by Thermo Fisher Scientific using a moulding temperature of 80 °C, a loading cylinder temperature of 200 °C, an injection pressure of 600 bar (10 s) and a post-injection pressure of 400 bar (10 s). All configurations were reprocessed up to 7 times and specimens for testing were collected at the 1st, 2nd, 3rd, 5th and 7th

reprocessing cycle.

2.2 Morphological and microstructural characterization

The evolution of fibre length distribution for the different composites was studied for increasing reprocessing cycles by immersing the specimens in tetrachloroethylene at 120 °C to dissolve PP. The suspended fibres were collected on a glass plate and their length measured with the optical microscope Leica DMI 5000. XRD analysis was performed with a X'Pert PRO diffractometer using a range of $2\theta = 10°–45°$, a CuKα monochromatic radiation (40 kV–40 mA), a 3 s time per step and a step size of 0.02°.

2.3 Thermal characterization

TGA was performed with a TG209 F1 Libra by Netzsch using a nitrogen atmosphere and heating from room temperature to 800 °C with a ramp of 10 °C/min.

DMA was performed with a DMA 242 E Artemis by Netzsch on 60 mm long, 10 mm wide and 4 mm thick samples using a 3-point bending configuration. Tests were carried out from -100 °C to 130 °C with a ramp of 2 °C/min, an amplitude of 30 μm and a frequency of 1 Hz.

DSC was carried out with a DSC 214 Polyma by Netzsch in a nitrogen atmosphere and a temperature range from -70 °C to 220 °C with a heating/cooling ramp of 10 °C/min.

The melt volume flow rate (MVR) was evaluated with an extrusion plastometer Mflow by Zwick/Roell using a fixed temperature of 230 °C, a sample pre-heating of 300 seconds and a load of 2.16 kg.

2.4 Mechanical characterization

Tensile, three-point bending and Charpy impact tests were performed to mechanically characterize the different configurations at the different reprocessing cycles.

Tensile and three-point bending tests were carried out with a Zwick/Roell Z010 machine employing a 10 kN load cell. Tensile tests were carried out on dog-bone shaped specimens with a 30 mm gauge length, a 5 mm width of the gauge length and a 1.5 mm thickness applying a preload of 1 MPa and a test speed of 5 mm/min. Three-point bending tests were performed on rectangular specimens with a 80 mm length, a 10 mm width and a 4 mm thickness with a 64 mm span length, a 5 mm/min test speed and a preload of 1 MPa.

Charpy impact tests were carried out in an Instron Ceast 9340 drop weight tower on rectangular specimens with a 80 mm length, 10 mm width and 4 mm thickness engraved in the middle with a type-A V shaped notch (tip radius of 0.25 mm). An edgewise sample orientation, a 62 mm span length, a 13.5 J energy and 2.9 m/s velocity were selected. Tests were performed at room, +50 °C and -50 °C, to assess the effect of temperature. Specimens were preconditioned for 1 hour at the operating temperature.

A fracture surface analysis was carried out with a FEG-SEM Mira3 by Tescan on both tensile and Charpy impacted samples to evaluate the effect of reprocessing cycles on composites damage mode.

3 RESULTS AND DISCUSSION

3.1 TGA and DMA

No significant changes were observed in the TGA and DMA response of all configurations under study as a consequence of mechanical reprocessing. Both neat PP and compatibilized PP are characterized by a degradation temperature at around 458 °C regardless of the number of reprocessing cycles, because polyolefins degrade by radical random scission which is not affected by macromolecules length reduction induced by mechanical reprocessing. Similar outcomes were observed for basalt composites where the inert reinforcement does not modify the thermal degradation behaviour of the original matrix. An increase of few degrees in PP temperature degradation was detected in flax and hybrid composites due to flax fibres presence which undergo thermal degradation already at 353-363 °C and absorb a conspicuous part of the heat thus delaying PP degradation onset.

Similarly, no significant changes were detected in the glass transition temperature of all composites for increasing reprocessing cycles with a value between -34.5 °C and -29.2 °C for the glass transition calculated from the storage modulus and between -6.3 and -1.7 °C for the one calculated from tanδ.

3.2 XRD and DSC

Coherently with the other thermal analyses, no significant variations in melting temperature, crystallization temperature and crystallinity degree were observed for increasing reprocessing cycles, while some variations were detected among the different formulations under study. Neat PP displays a crystallinity degree slightly higher, i.e., of around 5%, than compatibilized one due to the maleic anhydride bulky groups which break the matrix molecular chains regularity and reduce their ability to pack efficiently. This conclusion is further corroborated by the small decrease in MAPP crystallization temperature and by the disappearance of the orthorhombic γ phase in its crystalline structure observed with the XRD analysis. Considering all composites, the introduction of the fibre reinforcement allows to increase the MAPP crystallinity degree reaching values comparable or even higher than neat PP ones thanks to the nucleating effect played by the natural fibres surface.

3.3 Fibres length distribution

Extrusion is a manufacturing process highly detrimental to fibre reinforcements which undergo a significant reduction in length due to the high viscosity of the molten mass and to the friction phenomena which arise between fibres and as a consequence of the interaction with the extruder screw. In light of this, the study of fibre length as a function of the number of reprocessing cycles is fundamental to understand the resulting effect on composites mechanical performance. Figure 1 reports the average fibre length after all the reprocessing cycles for all flax, basalt and hybrid composites. All fibres, regardless of composite formulation, are characterized by a progressive decrease in average length which is combined with a progressive narrowing of the distribution curve caused by the disappearance of the longest fibres.

Basalt fibres display a much higher decrease in the average length compared to flax due to their stiffer and brittle nature which makes them prone to the bending moments resulting from the flowing of the molten mass. Basalt fibres experience a higher decrease in their length during the first reprocessing cycles because the progressive reduction of their length makes them more prone to bending moments which are directly proportional to this parameter. The latter outcome must be also ascribed to polymer viscosity decrease which reduces the load applied on the fibres and the resulting bending moment.

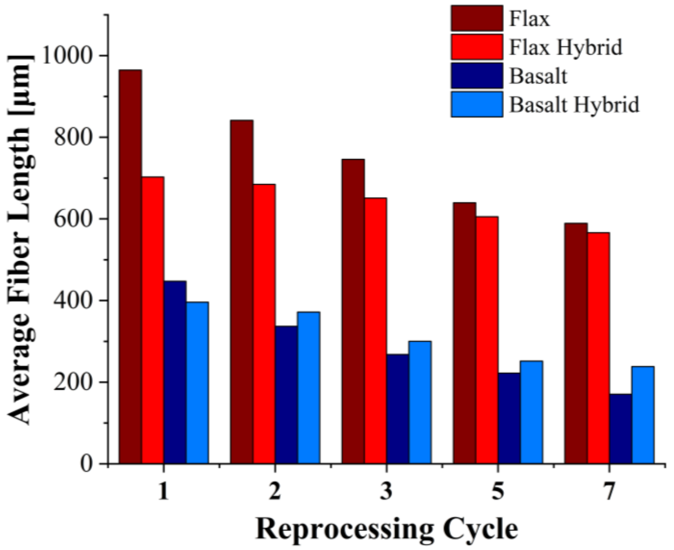

Figure 1: Average fibre length of flax, basalt and hybrids as a function of the number of reprocessing cycles

If basalt fibres in both basalt and hybrid composites displayed a comparable trend, more interesting results can be highlighted for flax fibres. Indeed, flax fibres interaction with basalt is responsible for a stronger length reduction due to basalt fibres acting as pins which promote flax fibres fibrillation. Flax fibres in flax composites show a smaller decrease in length because fibrillation phenomena are diluted throughout all reprocessing cycles.

3.4 MVR

If TGA, DMA and DSC highlighted no significant effect of mechanical recycling on the thermal behaviour of the formulations under study, different outcomes were obtained for the MVR index which experiences conspicuous variations among the different reprocessing cycles as shown in Figure 2.

Compatibilized PP always displays a higher MVR than neat PP because of the intrinsic higher MFR (Melt Flow Rate) of the additive. Despite this, both matrices are characterized by a MVR increase for increasing reprocessing cycles due to the progressive scission of the macromolecules which results in molecular weight and melt viscosity reduction. Both polymers show a faster degradation for increasing reprocessing cycles.

Both flax and hybrid composites are characterized by a significantly lower MVR due to the introduction of the fibrous reinforcement and, as the polymeric matrix, display a progressive increase in this index for increasing reprocessing cycles due to fibre length reduction. In particular, flax composites display the lowest MVR because of the higher fibre volume fraction and display almost a logarithmic increase in MVR with a steep increase in the first reprocessing cycles and a subsequent flattening of the values. This tendency can be directly correlated to results obtained for flax fibres length reduction which displayed a logarithmic decrease.

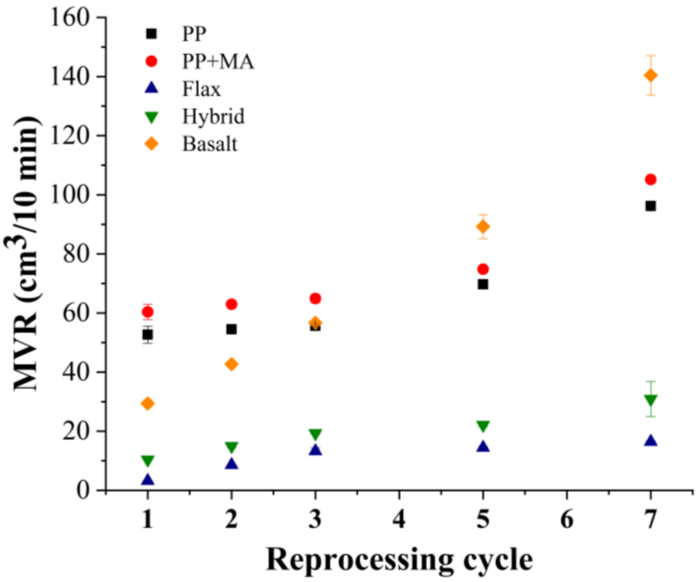

Figure 2: MVR index for formulations under study as a function of the number of reprocessing cycles

Different is the trend for hybrids where a linear increase in MVR can be detected and even in this case the tendency can be directly correlated to fibre length. Flax fibres in hybrids suffers a strong length reduction already after the first processing cycle displaying a length comparable to only flax composites after the third reprocessing cycle. Considering that the increase in flax composites MVR is quite low from the third to the seventh cycle, it can be assumed that flax fibres length reduction plays a minor role in hybrid and that hybrid MVR linear increase can be mainly ascribed to basalt fibres length reduction. This is further confirmed by basalt composite MVR trend which displays a steep increase with values higher than neat matrices ones at the fifth and seventh reprocessing cycles.

3.5 Tensile, bending and Charpy impact tests

Figures 3 and 4 show the tensile and flexural properties of the five configurations considered as a function of the number of reprocessing cycles, respectively.

Both neat and compatibilized PP matrices display a slight decrease in their mechanical performance due to mechanical reprocessing which probably causes a progressive molecular weight reduction of the polymer.

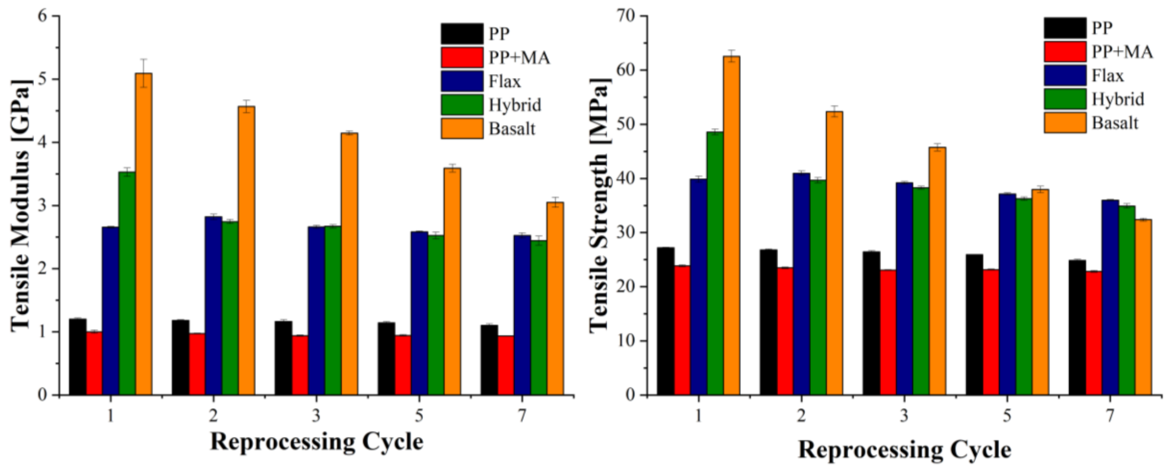

Figure 3: Tensile modulus and strength of the different configurations at the different reprocessing cycles

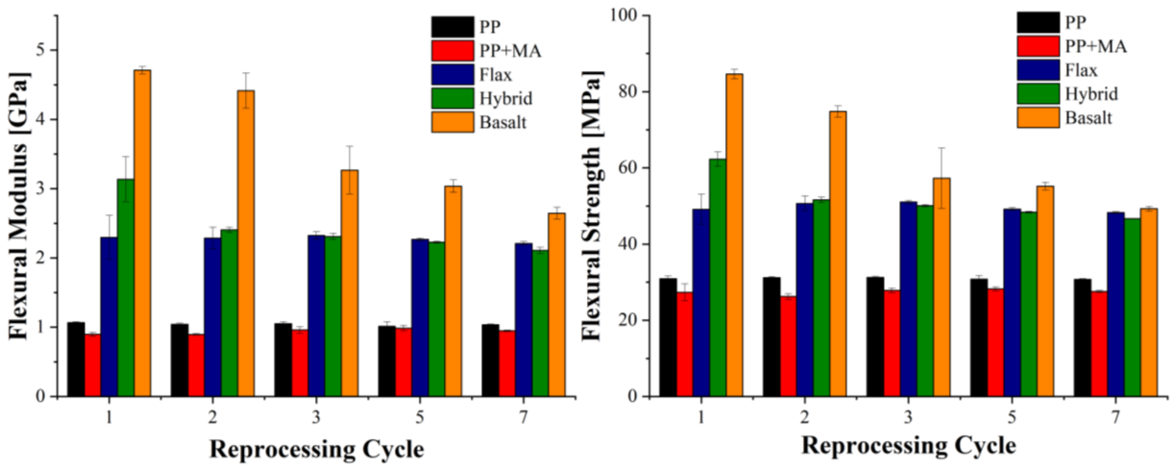

Figure 4: Flexural modulus and strength of the different configurations at the different reprocessing cycles

Focusing on the composites, basalt and flax composites display the highest and the lowest mechanical performance after the first processing cycle, respectively. Hybrids allow the achievement of intermediate mechanical properties thus confirming the potential of this technique to improve the mechanical output of bio-based composites while ensuring satisfying mechanical performance.

Flax composites display almost constant mechanical performance up to the seventh reprocessing cycle with a decrease lower than 10 % in tensile strength and this is ascribable to fibre fibrillation which keeps almost unaffected fibre aspect ratio. Basalt composites still display better tensile and flexural properties than flax and hybrid ones at the third reprocessing cycles but experience a huge drop after further reprocessing steps. Finally, hybrids experience a significant level off after the second reprocessing cycle with mechanical properties comparable with only flax composites.

Basalt and hybrid behaviour must be ascribed to the progressive decrease in basalt fibre length which is the load bearing component of the composite. This decrease in fibre length results in a strong decrease in fibre aspect ratio being constant the diameter of basalt fibres, thus making the reinforcement progressively ineffective.

Quasi-static characterization was flanked by Charpy impact characterization assessing the effect of both reprocessing cycles and operating temperature. All configurations experience a significant drop in impact strength when moving from +50 °C to -50 °C due to matrix glass transition overstepping which is at around -30 °C. Both neat and compatibilized matrices experience the highest drop in impact strength while the composites display a lower sensitivity due to the intrinsic higher brittleness deriving from the introduction of the fibrous reinforcement.

After the first reprocessing cycles, composites impact strength displays the same trend already observed for tensile and flexural tests with basalt being characterized by the best performance, flax by the worst and hybrids by an intermediate behaviour. Even in this case, hybrids experience a significant level off of their performance, but proved to be more performing than flax composites up to the third reprocessing cycle. Even in this case, this can be ascribed to the progressive reduction in fibres length which decreases the energy amount dissipated by fibre pull out.

4 CONCLUSIONS

The present work investigated the effects of mechanical recycling on bio-based composites produced with flax, basalt and flax/basalt hybrid fibres, evaluating the evolution of their microstructural, thermal and mechanical behaviour up to seven reprocessing cycles. The main outcomes are:

- The interaction of flax and basalt fibres in hybrids leads to a faster decrease in flax fibres length due to basalt fibres acting as pins which promote fibrillation phenomena.
- Hybrids are able to ensure better mechanical performance than flax composites in tension, bending and impact after the first reprocessing cycle, but experience a significant levelling already at the second reprocessing cycle while basalt composites remain competitive up to the third reprocessing cycle.
- Significant differences can be observed in the MVR value evolution with increasing reprocessing cycles for the three different classes of composites, with flax displaying the lowest increase in MVR and basalt displaying the highest one. Hybrids display an intermediate behaviour with a higher MVR provided by the partial substitution of flax fibres with basalt ones, but always showing a flax-fibre driven behaviour. The higher the MVR, the easier the re-processability of the composites.

In conclusion, both hybrids, which are usually designed to ensure higher mechanical performance than flax ones, and basalt composites can be mechanically recycled repurposing the material to produce components traditionally made with flax fibres. This allows to take advantage of recycled materials with slightly higher mechanical properties after the second and third reprocessing cycle and endowed with an easier processability.

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