

Basalt/polypropylene composites: The effects of mechanical reprocessing on their morphological, thermal, rheological and mechanical behavior

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ABSTRACT

Considering the increasing spread of basalt fibers on the market as bio-based alternative to glass and the massive use of polypropylene (PP) in the automotive sector, the end-of-life of PP/basalt composites through mechanical reprocessing was addressed. Their thermal, rheological and mechanical properties were investigated up to seven reprocessing cycles and the main relationship between their changes and composites fibers length reduction was disclosed. The composites displayed a parabolic increase in their melt volume rate for increasing reprocessing cycles and were characterized by an improved flowability compared to the neat matrix at the fifth cycle, i.e., 89.3 against 74.8 cm³/10min, due to the intimate contact between the fibers and the matrix which causes a stronger degradation in PP molecular weight. Concerning the mechanical response, the logarithmic decrease in stiffness and strength was not directly proportional to fibers length reduction due to a progressive better orientation of the fibers along the injection direction. Finally, the comparison of the mechanical results obtained with the data available for PP composites reinforced with vegetable fibers allowed to conclude that PP/basalt composites are competitive with this type of composites up to the fifth cycle, displaying a tensile modulus of 3.5 GPa and tensile strength of 38 MPa.

1. Introduction

Mass production of glass fibers started in 1893 [1] and experienced a significant growth during World War II when the search for lighter structures and for materials transparent to radio frequencies together with the development in unsaturated polyester resin production acted as driving force for the development of polymer composite materials [2,3]. Since then, glass fibers dominated polymer composites market accounting for more than 95 % of the total amount of fiber reinforcements used at an industrial scale [4]. Despite the lower specific mechanical properties than carbon fibers, glass fibers are considerably cheaper than carbon fibers thus being the preferred choice for the automotive industry, allowing to obtain a significant reduction in vehicles weight and in the related fuel consumption while maintaining a reasonable cost of the final product.

Despite all the advantages of glass fibers, the increasing environmental concerns deriving from global warming and wastes accumulation encouraged greener policies and the exploitation of eco-friendlier materials. In particular, the 2008/1/EC directive in the field of Integrated Pollution Prevention and Control (IPPC) promotes the

exploitation of materials from renewable resources. In light of this, many efforts were made to identify a valid alternative to glass fibers and a suitable solution was identified in basalt fibers.

Basalt is a natural material found in volcanic rocks originated from frozen lava and it was first produced at an industrial scale in 1985 [5]. From the mechanical performance perspective, it is characterized by tensile properties higher than E-glass fibers [6] and, despite a slightly higher density, by comparable specific mechanical properties [5]. From the manufacturing perspective, the process for basalt fibers production is similar to glass fibers [5,7], thus ensuring a good adaptability of the industrial plants already available with low investment costs. The lower energy consumption and absence of chemicals and additives addition during the manufacturing process make basalt an eco-friendlier choice compared to glass fibers [5,7]. This is confirmed by the life cycle assessment (LCA) study performed by Ghali et al. [8] where basalt fibers displayed a lower global warming potential, with a 2.19 kg of CO₂-eq emissions against the 3.43 kg of glass fibers, and a lower acidification of water and soil, with a 0.01 kg of SO₂-eq emissions against the 0.02 kg of glass fibers.

However, basalt fibers are non-biodegradable as glass ones and this

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makes the identification of suitable end-of-life strategies necessary. The 1999/31/EC regulation encompassed in the 2008/1/EC directive deters the use of landfills and promotes materials reuse and recycling in a circular economy perspective [9]. Among the recycling paths available for thermoplastic polymer and polymer composites wastes, i.e., mechanical, chemical and thermal recycling, mechanical reprocessing is the one characterized by the lowest environmental impact [10–12]. Despite this, mechanical reprocessing of polymer composites causes a progressive decrease in the overall fibers length which can significantly jeopardize the mechanical performance of the resulting component. In light of this, the study of fibers length, thermal, rheological and mechanical properties evolution as a function of the number of reprocessing cycles plays a fundamental role for short fiber reinforced polymer composites (SFRPCs).

Considering the restrictions imposed to the transportation sector by the 2000/53/EC regulation, many studies focused on the mechanical recycling of polypropylene (PP) composites. PP is the most widely used thermoplastic polymer in the automotive sector accounting for more than 30 % in 2021 according to the data reported by Grand View Research [13]. It is applied in dashboard, pillar trim, doors and seat carriers, but it is also largely exploited as matrix for polymer composites [14].

The first researches in this direction focused on PP/glass fiber composites. Colucci et al. [15] highlighted a decrease of 18.7 and 27.5 % in flexural strength and of 13.7 and 23.8 % in tensile strength for 50 % and 100 % recycled PP/glass fibers composites when compared with the pristine material. Krzyzak et al. [16] studied the shrinkage behavior of PP/glass fiber composites before and after reprocessing and highlighted a decrease in the shrinkage of reprocessed specimens compared to first processed ones. Evens et al. [17] investigated the influence of ten reprocessing cycles on the mechanical properties of different PP composites reinforced with glass and carbon fibers. They disclosed a strong reduction in fibers length for both composites types for increasing reprocessing cycles, with corresponding decrease of 50 and 25 % in tensile strength and of 45 % and 35 % in flexural modulus after the 10th reprocessing cycle for glass and carbon fibers reinforced composites, respectively.

The introduction of vegetable fibers in the automotive sector for the production of non-structural components, i.e., door panels, trays, package shelves, etc. [18], made the investigation of their response to recycling also necessary. Jubinville et al. [19] and Beg and Pickering [20] investigated the mechanical reprocessing of wood PP-based plastic composites up to the 6th and 8th cycle, respectively. In particular, Beg and Pickering [19] reported a reduction of 25 % in tensile strength, of 16 % in tensile modulus, of 21 % in flexural modulus, of 30 % in flexural strength, and of 41 % in impact strength at the last reprocessing cycle. Similar studies were carried out on PP/flax composites [17,20], PP/sugarcane bagasse composites [21] and PP/rice hulls and PP/kenaf composites [22]. Finally, a study by Sergi et al. [23] investigated the influence of mechanical recycling up to seven reprocessing cycles on flax and basalt hybrid PP composites and reported that the interaction of flax and basalt fibers determines an accelerated degradation of flax fibers length causing a significant drop in hybrid mechanical performance already at the 2nd reprocessing cycle.

Despite many studies are available on SFRPCs mechanical recycling [24], only one of them focused on basalt fibers. In particular, Finnerty et al. [25] studied the mechanical reprocessing up to six cycles of polylactic acid (PLA)/basalt composites. Despite this, no works on PP/glass fiber composites provided a relationship between fibers length reduction and mechanical properties decrease. Considering this, the present work focused on disclosing the main relationship between composites microstructure, i.e., fibers length, and their mechanical performance up to seven reprocessing cycles. Moreover, the evolution of the rheological behavior of PP/basalt composites with increasing reprocessing cycles was also investigated and this aspect was never assessed before. Even in this case, a relationship between composites complex viscosity decrease

and fibers length reduction was provided.

Composites morphology and microstructure were analyzed through fiber length measurement, circularity analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Composites thermal behavior was investigated through thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), rheological studies and Melt Volume Flow Rate (MVR). Finally, the mechanical properties of PP/basalt composites were evaluated through tensile, 3-point bending and Charpy impact tests as a function of reprocessing cycles.

2. Materials and methods

2.1. Materials and composite manufacturing

Isplen PP094 by Repsol with a density of 0.905 g/cm³ was selected as polypropylene matrix. Short basalt fibers provided by Incotology GmbH with a nominal length of 6.4 mm and an average diameter of 13 µm were used as reinforcement. In particular, an amount of 30 wt% of basalt fibers was used for composites manufacturing. Moreover, a 5 wt% of standard maleic anhydride grafted polypropylene (MAPP) was added to the master batch to improve fiber/matrix interfacial adhesion. In particular, the Polybond 3200 provided by Addviant Corporation and characterized by a high maleic anhydride content (0.8–1.2) was selected.

The Thermo Scientific Process 11 co-rotating twin screw extruder with eight different heating zones was used to compound the composites. A 150 rpm screw speed was used and the following temperature profile was selected: 185–190–200–210–210–200–200–200 °C. The temperature profile was selected following the melt temperature range, i.e., 190–250 °C, advised by the supplier. Matrix pellets and basalt fibers were dry blended and fed, without pre-heating, into the main hopper during compounding. A Haake MiniJet II Pro by Thermo Fisher Scientific was used to inject the resulting compound using a 200 °C loading cylinder temperature and a 80 °C molding temperature. During the injection phase, a first step performed with an injection pressure of 600 bar for 10 s allowed for compound flow into the mold while the second post-injection step performed with a holding pressure of 400 bar for 10 s allowed to prevent specimens' shrinkage.

PP/basalt composites were reprocessed up to seven times and the samples required to perform the morphological, thermal, rheological and mechanical campaign were collected at the 1st, 2nd, 3rd, 5th and 7th cycle. A pelletizer was used to carry out the mechanical reprocessing in order to produce pellets easily feedable again into the extruder. In particular, part of the processed material was allocated for samples' production after the initial compounding by loading directly the injection molding cylinder with the molten polymer, while the remaining part of the extrudate was air-cooled, pelletized and further processed. This operation was repeated for each reprocessing cycle. A schematization of the overall process is provided in Fig. 1.

2.2. Microstructural and morphological characterization

Considering that SFRPCs mechanical behavior strongly depends on fibers length, the evolution of their length distribution was evaluated and monitored throughout the reprocessing cycles. All basalt composites were immersed in tetrachloroethylene at 120 °C to dissolve the PP matrix [26] and a glass plate was used to place the suspended fibers obtained. An optical microscope Leica DMI 5000 was used to determine fibers length and at least 500 fibers were measured for each sample.

A qualitative circularity analysis was performed to evaluate fibers orientation with respect to the injection direction and to disclose potential variation for increasing reprocessing cycles. Specimens were cut perpendicularly to the injection direction and were embedded in the bicomponent epoxy resin Epothin 2 by Buehler using a resin: hardener ratio of 2:1. After 24 h at room temperature necessary to achieve resin

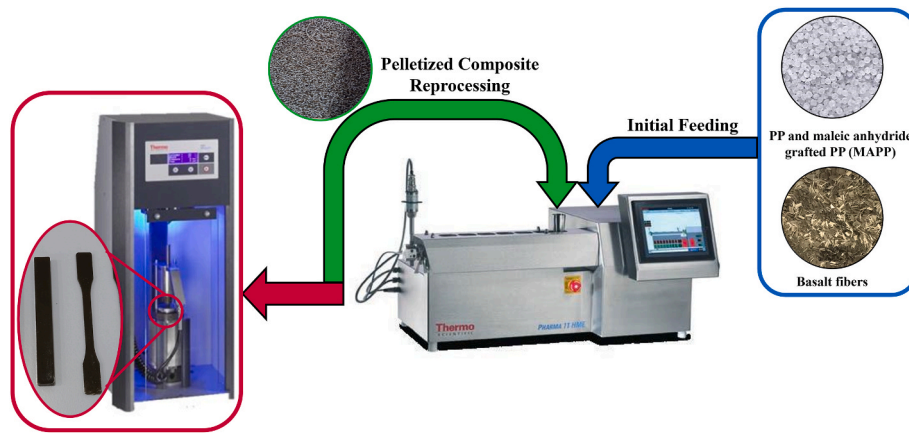


Fig. 1. Schematization of the overall manufacturing process.

hardening, samples were polished with the Mecatech 334 polishing machine by Presi using a rotation speed of 150 rpm for the plate and of 100 rpm for the carousel containing the specimens and an overall force of 0.5 daN. The carousel and the plate worked in a co-rotating mode. In the first phase of polishing, sandpapers with progressive grits of 800, 1200, 2500 and 4000 were used. Two sandpapers per type were used and each sandpaper was used twice for 3 min' cycles. After sandpapers polishing, specimens were polished with 9, 6 and 1 μm diamond polishing suspensions for cycles lasting 20 min. The polished samples were analyzed with the optical microscope Leica DMI 5000.

X-ray diffraction (XRD) was used to identify the typical crystalline structure of the PP matrix and to highlight potential changes deriving from the mechanical reprocessing. A X'Pert PRO diffractometer was used for the analysis and the diffraction spectrum was collected in the $2\theta = 10^\circ\text{--}45^\circ$ range using a $\text{CuK}\alpha$ monochromatic radiation, applying a 40 kV voltage, a 40 mA current, a 3 s time per step and a step size of 0.02° .

2.3. Thermal characterization

PP/basalt composites thermal stability was studied through TGA according to ISO 11358 using a TG209 F1 Libra by Netzsch. Tests were carried out using a heating ramp of $10^\circ\text{C}/\text{min}$ from room temperature to 800°C in a nitrogen atmosphere.

DMA was performed according to ISO 6721 using the DMA 242 E Artemis by Netzsch. Rectangular specimens with a length of 60 mm, a width of 10 mm and a thickness of 4 mm were tested in a temperature range from -100°C to 130°C using a 3-point bending configuration. A span length of 40 mm, a heating ramp of $2^\circ\text{C}/\text{min}$, an amplitude of 30 μm and a frequency of 1 Hz were selected as operating parameters.

DSC tests were carried out according to ISO 11357 using a DSC 214 Polyma by Netzsch. A temperature range from -70°C to 220°C was used to test the specimens and a heating/cooling/heating ramp of $10^\circ\text{C}/\text{min}$ was applied in a nitrogen atmosphere. A first heating ramp was applied to all samples to remove their thermal history and the data resulting from the cooling and the second heating scans were exploited for the analysis. Polypropylene crystallinity was calculated according to Equation (1):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_{m0} (1 - w_f)} * 100$$

where ΔH_m is the melting enthalpy calculated from the DSC curve, ΔH_{m0} is the melting enthalpy of a fully crystalline PP matrix ($\Delta H_{m0} = 207 \text{ J/g}$) [27] and w_f is the fibers weight fraction.

The melt volume flow rate (MVR) of reprocessed composites was evaluated according to ISO 1133 using an extrusion plastometer Mflow by Zwick/Roell. A load of 2.16 kg was applied, the cylinder temperature

was set at 230°C and the samples inside the cylinder were pre-heated for 300 s. Three samples were tested for each configuration and reprocessing cycle.

2.4. Rheological characterization

The dynamic rheological behavior of PP/basalt composites was assessed through frequency sweep tests in the range from 0.1 to 100 rad/s at 190°C by using an ARES G2 rheometer by TA instruments in parallel plate geometry. A plate diameter of 25 mm and a gap of 1 mm were used. The strain amplitude was fixed at 5 %, which is within the linear viscoelastic region as established from preliminary strain sweep tests. The tests were performed in triplicate.

2.5. Mechanical and morphological characterizations

The mechanical performance of PP/basalt composites was investigated by quasi-static three-point bending and tensile tests and by dynamic Charpy impact tests.

A Zwick/Roell Z010 universal testing machine was used to perform both tensile and three-point bending tests employing a 10 kN load cell. Rectangular samples ($80 \times 10 \times 4 \text{ mm}$) were used for the three-point bending tests and at least three specimens were tested for each reprocessed configuration. The tests were carried out according to ISO 178 applying a preload of 1 MPa, a span length of 64 mm and a test speed of 5 mm/min . Dog-bone shaped samples with a 30 mm gauge length, a 5 mm width and a 1.5 mm thickness were used to perform the tensile tests according to ISO 527-2 and at least five specimens were tested for each reprocessed configuration.

An instrumented Instron/Ceas 9340 drop weight tower was used to perform Charpy impact tests according to ISO179-2. Notched rectangular samples ($80 \times 10 \times 4 \text{ mm}$) were used to perform the tests. A type-A notch characterized by a tip radius of 0.25 mm was employed according to ISO179-1. Specimens were tested with a velocity of 2.9 m/s and 13.5 J energy using a span length of 62 mm and edgewise orientation. The effect of temperature was also investigated by performing the tests at room temperature, i.e., 23°C , $+50^\circ\text{C}$ and -50°C . A 1-h preconditioning at the operating temperature was applied to all specimens to ensure a homogenous temperature profile throughout the specimen. At least three specimens were tested for each configuration and temperature.

Moreover, fracture surface analysis was carried out on both failed tensile and Charpy impact specimens to study composites damage mode. Fracture surfaces were sputter-coated with gold to prevent charging and were analyzed with a FEG-SEM Mira3 by Tescan.

3. Results and discussion

3.1. Fibers length distribution

It is well known that the mechanical properties of SFRPCs strongly depend on the length of the reinforcing fibers which must overcome the critical length value to effectively act as a reinforcement. It is also universally acknowledged that extrusion and injection molding, i.e., the two most common techniques to produce SFRPCs, cause a strong reduction in the length of fibers. The bending moment applied by the polymeric flowing melt [28], the friction phenomena arising from fiber-screw and fiber-fiber interactions [29] and the high velocities applied to inject the polymeric mass in the mold [30] are all responsible for the strong decrease in fibers length. In light of this, basalt fibers length distribution as a function of the number of reprocessing cycles was investigated and the results obtained are reported in Fig. 2.

Basalt fibers display a progressive decrease in their average length for increasing reprocessing cycles and this trend can be described by a logarithmic interpolation curve with a $R^2 = 0.996$. In particular, basalt fibers experience a decrease in length of 24.7 % from 447.4 μm to 336.8 μm between the first and the second cycle, of 20.5 % from 336.8 μm to 267.7 μm between the second and the third cycle, of 17.1 % from 267.7 μm to 221.9 μm between the third and the fifth cycle and of 23.1 % from 221.9 μm to 170.6 μm from the fifth to the seventh cycle. A faster decrease in fibers length during the first reprocessing cycles was noted, and this can be ascribed to their stiff and brittle nature which make them extremely prone to the bending moments exerted by the flowing melt. In particular, bending moments experience a progressive decrease for increasing reprocessing cycles because they are directly proportional to basalt fibers length and the lower the fiber length, the lower the bending moment they are subjected to. Moreover, the progressive decrease in polymer mass viscosity, which will be discussed in section 3.5, is also responsible for bending moment reduction being lower the load that it is able to apply on the fibers.

Another important outcome concerns the progressive narrowing of basalt fibers distribution curves for increasing reprocessing cycles resulting from the progressive loss of the longest fibers. This phenomenon was easily inferred from the decrease in the standard deviation values resulting from the Gaussian curves interpolation. In particular, standard deviation values of 190.7 μm , 188.2 μm , 114.4 μm , 88.4 μm and 70.2 μm were observed after the first, second, third, fifth and seventh reprocessing cycles, respectively.

3.2. TGA analysis

The thermal stability of PP/basalt composites as a function of the number of reprocessing cycles was investigated by TGA. Fig. 3 shows the representative TGA and DTG curves of the composites at the first, third

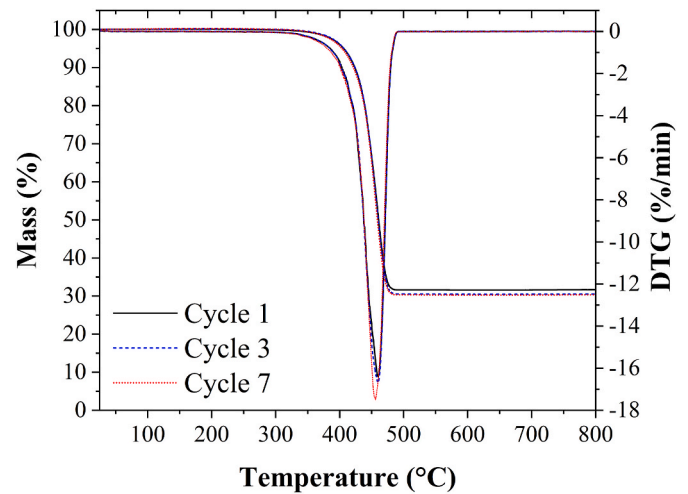


Fig. 3. TGA and DTG curves of PP/basalt composites at the first, third and seventh reprocessing cycle.

and seventh reprocessing cycle, while Table 1 summarizes the residual basalt fibers content and the degradation temperatures calculated at the point where the degradation rate is maximum, i.e., at the minimum point in the DTG curves.

No significant variations can be observed in TGA and DTG curves nor in the degradation temperature for increasing reprocessing cycles in accordance with the results reported for neat and recycled PP by Colucci et al. [15], by Sergi et al. [23] and by Gall et al. [31]. Indeed, basalt fibers are thermally stable in the temperature range investigated and the single degradation temperature observed must be ascribed to PP. This constant thermal degradation behavior, irrespective of the number of reprocessing cycles, must be ascribed to the inherent thermal behavior of polyolefins which degrade in a single step through radical random chain scission [32]. This phenomenon is likely not affected by the progressive reduction in macromolecules length induced by mechanical reprocessing.

Table 1

Composites degradation temperatures calculated by the DTG curves and residual fibers content.

Sample	PP Degradation Temperature (°C)	Basalt Fibers Content (%)
PP/Basalt_Cycle1	459.5 \pm 1.6	34.2 \pm 1.2
PP/Basalt_Cycle2	460.1 \pm 1.0	31.6 \pm 1.0
PP/Basalt_Cycle3	460.0 \pm 0.8	30.5 \pm 0.6
PP/Basalt_Cycle5	457.0 \pm 1.0	30.2 \pm 0.8
PP/Basalt_Cycle7	456.0 \pm 0.9	30.2 \pm 0.8

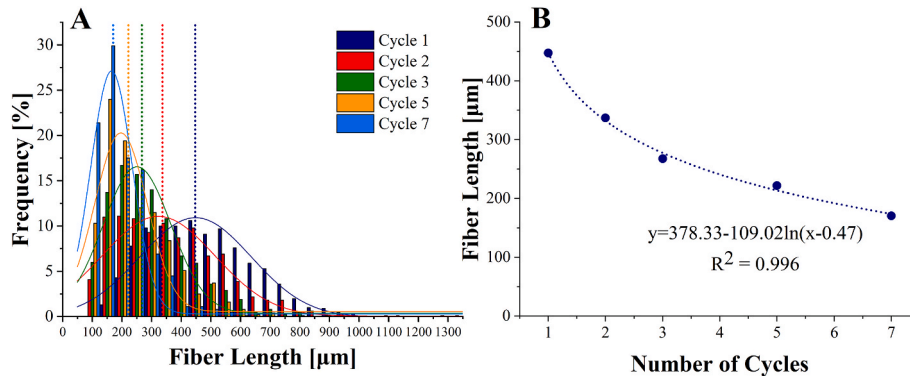


Fig. 2. Basalt fibers length distribution in PP composites as a function of the number of reprocessing cycles with relative average values (dot lines) and interpolation distribution (solid lines) [A]. Average basalt fibers length trend as a function of the number of reprocessing cycles [B].

Composites with a theoretical 30 wt% of basalt fibers were manufactured and TGA results allowed to conclude that the manufacturing process resulted in a good control of reinforcement amount with fiber weight percentages close to the theoretical target.

3.3. DSC and XRD analysis

The melting and crystallization behaviors of PP/basalt composites as a function of the reprocessing cycles were investigated through DSC and XRD. Fig. 4 shows the heating and cooling DSC curves and the XRD spectra of PP/basalt composites at the first, third and seventh reprocessing cycles, while Table 2 summarizes the melting and crystallization temperatures and the degree of crystallinity at each cycle.

The melting and crystallization temperatures of PP/basalt composites, as the thermal degradation behavior, are not affected by mechanical reprocessing. Slight variations can be detected only in the crystallization behavior for increasing reprocessing cycles where a narrowing and sharpening of the crystallization peak can be observed. This can be likely ascribed to a progressive decrease in PP molecular weight which is connected to a decrease in macromolecules length thus making crystallization easier and more concentrated in a restricted temperature range. These results are coherent with the ones by Paukkeri and Lehtinen [31], who reported that PP molecular weight has a slight effect on crystallization rate, but almost no influence on the overall crystallinity.

These conclusions are further corroborated by the XRD spectra where no significant changes in PP diffraction peaks can be detected moving from the first to the seventh cycle. Diffraction peaks at 14.00° , 16.85° , 18.55° , 21.0° , 21.80° , 25.40° , 28.40° and 42.60° were identified and they can be associated with the (110), (040), (130), (111), (041), (060) along with (150), (220) and (212) crystallographic planes of the monoclinic α crystalline structure, which is the most thermodynamically stable, respectively [33].

3.4. DMA analysis

The glass transition temperatures of the composites under study as a function of the number of processing cycles were evaluated through DMA. Two different glass transition temperature values were evaluated, i.e., one from the storage modulus and the other one from $\tan\delta$. In particular, the glass transition temperature from storage modulus curve was identified by the intercept of the two straight lines which are tangent to the glassy and to the drop transition regions. The glass transition temperature from $\tan\delta$ was obtained from the peak in the $\tan\delta$ curve. Fig. 5 shows the storage modulus and $\tan\delta$ curves for PP/basalt composites at the first, third and seventh reprocessing cycles while Table 3 summarizes the glass transition values evaluated for each configuration.

Again, as already reported for TGA and DSC, mechanical reprocessing does not seem to modify significantly the thermal behavior of PP/

basalt composites, with negligible differences in the glass transition temperatures for increasing cycles. Considering that semi-crystalline polymers glass transition temperature strongly depends on their crystallinity degree [34], the results are coherent with DSC ones where no significant variations in the crystallinity degree were observed.

3.5. MVR index and rheology

If the thermal analysis results reported up to now did not disclose a significant effect of mechanical recycling on PP/basalt composites thermal behavior, a strong dependence of their rheological behavior on the number of reprocessing cycles was observed.

At first MVR tests were performed and the results obtained for both PP/basalt composites and the neat compatibilized matrix are shown in Fig. 6 [A]. Both materials display a parabolic increase in MVR values for increasing numbers of cycles ($R^2 = 0.988$ for the neat matrix and $R^2 = 0.998$ for PP/basalt composites). For the pure matrix, this outcome can be likely correlated to a progressive decrease in polymer molecular weight deriving from macromolecules scission, which results in a reduction in polymer melt viscosity. This degradation phenomena must be ascribed to the combined effect of operating temperature and mechanical stresses during the extrusion and injection phases [35,36].

Concerning PP/basalt composites, they always display a parabolic increase in MVR values with mechanical reprocessing cycles, but they are characterized by a sharper increase in this parameter. In particular, MVR shows an increase of 45.3 % moving from the first to the second cycle, of 32.7 % from the second to the third cycle, of 57.4 % from the third to the fifth cycle and of 57.4 % from the fifth to the seventh cycle. This steeper trend in degradation can be ascribed to the combined effect of matrix degradation and fibers length reduction.

However, the most interesting result is that PP/basalt composites are characterized by a lower MVR value than the matrix alone at the first, second and third cycles, but the trend reverses at the fifth cycle where the composites start to display a higher MVR than the neat matrix. Indeed, it is universally acknowledged that the introduction of fillers inside a polymeric matrix leads to an increase in the melt viscosity [37] because they act as barriers which modify polymer flow lines thus restricting its chain mobility [38]. Therefore, the switch in MVR trend at the fifth cycle must be likely ascribed to a stronger degradation in polymer molecular weight resulting from the intimate contact with the basalt fibers and the related friction phenomena.

Even if MVR is directly correlated to melt rheology and polymers molecular weight, it does not provide a direct measure of viscosity and is just a punctual measurement that depends on test conditions. In light of this, rheological tests were performed to ensure a better insight in PP/basalt composites behavior and the resulting complex viscosity curves as a function of the angular frequency and of the number of reprocessing cycles are shown in Fig. 6 [B].

The flow curves of the PP/basalt composites exhibit a subtly more pronounced non-Newtonian behavior at low frequencies when

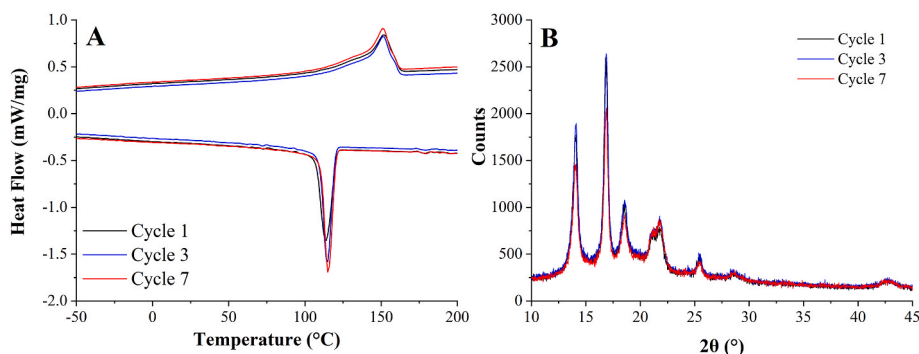
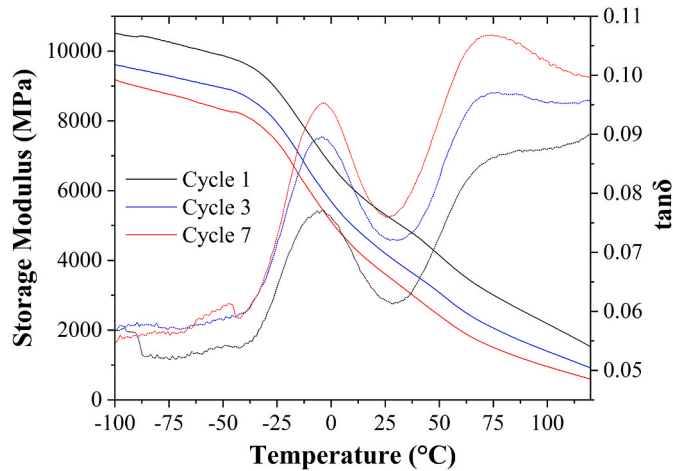


Fig. 4. DSC curves [A] and XRD spectra [B] of PP/basalt composites at the first, third and seventh reprocessing cycle.

Table 2

PP/basalt composites melting and crystallization temperatures and crystallinity degree for increasing reprocessing cycles.

Sample	Melting Temperature (°C)	Crystallization Temperature (°C)	Crystallinity Degree (%)
PP/Basalt_Cycle1	151.6 ± 0.2	113.7 ± 1.0	41.7 ± 0.9
PP/Basalt_Cycle2	152.8 ± 0.6	115.6 ± 0.6	42.6 ± 0.5
PP/Basalt_Cycle3	151.4 ± 0.2	114.6 ± 1.1	41.5 ± 0.7
PP/Basalt_Cycle5	151.2 ± 0.1	115.2 ± 0.5	43.3 ± 1.0
PP/Basalt_Cycle7	151.3 ± 0.1	115.1 ± 0.7	42.5 ± 0.8

**Fig. 5.** Storage modulus and $\tan\delta$ curves of PP/basalt composites at the first, third and seventh reprocessing cycle.

compared to the unfilled polymer, whose curves are reported in Fig. 6 [C]. As expected, these curves demonstrated a tendency to shift towards lower viscosity values with an increasing number of processing cycles. This outcome can be attributed to the degradation of PP chains, resulting in a reduction in the average molecular weight. Similar observations have been reported in the literature for other polypropylene-based systems undergoing multiple extrusion cycles [39].

Considering the paramount importance of polymer composites rheology to optimize the manufacturing process, the absolute values of fibers length and of complex viscosity at an angular frequency of 1 rad/s

for both PP/basalt composites and neat PP matrix after all reprocessing cycles were normalized with respect to their initial value after the first processing and the results obtained are reported in Fig. 7. An angular frequency of 1 rad/s was selected because low shear rates are needed to highlight potential differences in polymers microstructure.

As already pointed out in section 3.1, basalt fibers are characterized by a logarithmic decrease in their average length for increasing reprocessing cycles ($R^2 = 0.996$) and the same trend was also found for neat PP ($R^2 = 0.990$) and PP/basalt composites ($R^2 = 0.993$) complex viscosity. Up to the second reprocessing cycle, both matrix and composites complex viscosity are characterized by a comparable decrease which is also compatible with the decrease in fibers length experienced by the composites. The situation changes from the third reprocessing cycle where PP/basalt composites start to display a progressive more pronounced decline in complex viscosity compared to the one of the matrix alone.

This outcome allows to corroborate the conclusions drawn from the MVR results where two competing phenomena, i.e., matrix degradation and fibers length reduction, were identified as responsible for composites increased flowability. The steeper nature of the logarithmic curve of the composites compared to neat matrix viscosity and to the fibers length reduction, which are characterized by a superimposable trend, seems also to confirm the higher degradation experienced by the PP matrix due to the intimate contact with the basalt fibers, as already pointed out from the switch in MVR trend from the third to the fifth cycle.

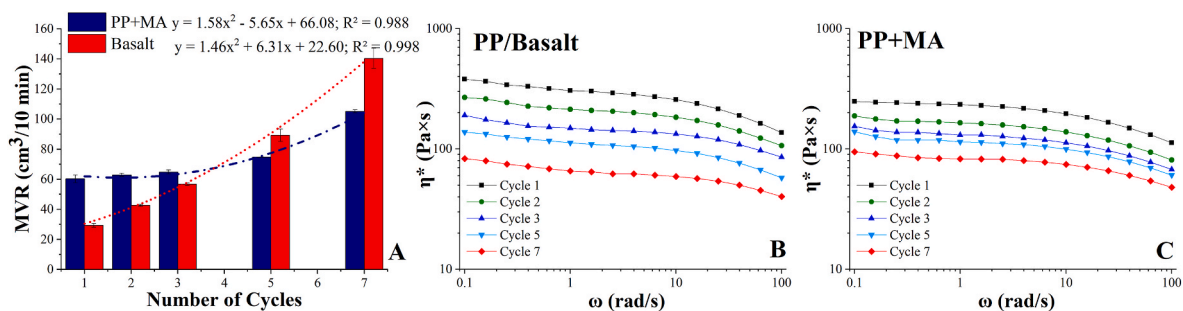
3.6. Quasi-static tensile and bending tests

The effect of mechanical reprocessing on PP/basalt composites mechanical properties was assessed through tensile and 3-point bending tests and the results obtained in terms of stiffness and strength are

Table 3

Glass transition temperatures of PP/basalt composites for all processing cycles.

Sample	Glass Transition Temperature from Storage Modulus (°C)	Glass Transition Temperature from $\tan\delta$ (°C)
PP/Basalt_Cycle1	-32.5 ± 0.5	-6.1 ± 0.7
PP/Basalt_Cycle2	-33.1 ± 0.7	-5.7 ± 0.4
PP/Basalt_Cycle3	-32.0 ± 0.8	-4.9 ± 0.8
PP/Basalt_Cycle5	-32.7 ± 1.0	-4.6 ± 0.9
PP/Basalt_Cycle7	-30.4 ± 1.2	-3.5 ± 0.9

**Fig. 6.** Experimental values and the related interpolation trend of MVR index [A] and rheological curves of PP/Basalt composites [B] and of the compatibilized PP matrix [C] as a function of the number of reprocessing cycles.

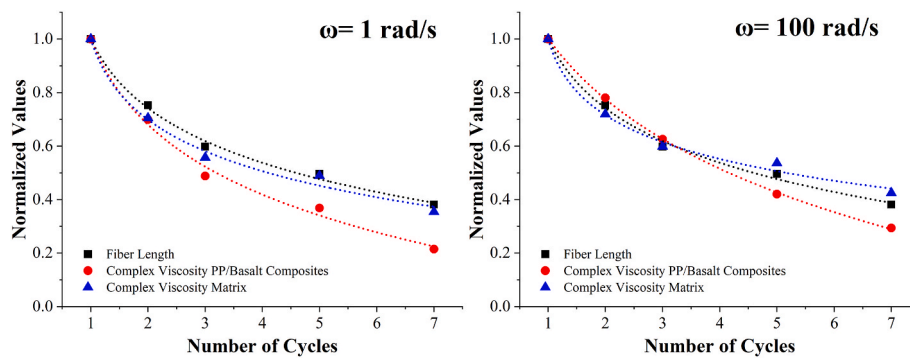


Fig. 7. Normalized values of PP/basalt composites fibers length and complex viscosity and of neat matrix complex viscosity as a function of the number of reprocessing cycles for an angular frequency of 1 rad/s.

reported in Fig. 8.

For both tensile and flexural performance a logarithmic decrease in stiffness and strength was observed for increasing reprocessing cycles ($R^2 = 0.998$ for tensile stiffness, $R^2 = 0.999$ for tensile strength, $R^2 = 0.923$ for flexural stiffness and $R^2 = 0.939$ for flexural strength). This means that the detrimental effect of mechanical reprocessing is more pronounced during the first cycles. Indeed, tensile stiffness decreases of 18.6 % from the first to the third cycle and of 15.1 % from the fifth to the seventh cycle while tensile strength decreases of 26.9 % from the first to the third cycle and of 14.6 % from the fifth to the seventh cycle. Analogously, flexural stiffness decreases of 30.6 % from the first to the third cycle and of 12.8 % from the fifth to the seventh cycle while flexural strength decreases of 32.3 % from the first to the third cycle and of 10.8 % from the fifth to the seventh cycle. This trend is directly related to basalt fibers length reduction which is also characterized by a logarithmic decrease for increasing reprocessing cycles.

To provide a direct correlation between composites tensile properties and fibers length, the absolute values of stiffness, strength and fiber length after all processing cycles were normalized with respect to their initial values after the first processing and the results obtained are reported in Fig. 9. Even if both stiffness and strength are characterized by the same logarithmic decrease experienced by fibers length, this type of analysis allowed to point out that there is not a direct proportionality between fibers length and mechanical properties reduction. Indeed, both stiffness and strength are characterized by a more gradual decline, thus meaning that a competing phenomenon intervenes to counterbalance fibers deterioration.

The latter was conveniently identified through the qualitative analysis of circularity shown in Fig. 10. Thanks to the progressive decrease in fibers length reported in section 3.1 and to the decrease in composites viscosity reported in section 3.5, an increasing number of fibers is able to orient itself along the injection direction which coincides with the tensile load direction. Therefore, the better orientation of the fibers allows

to partially counterbalance their reduction in length.

The results of quasi-static tests are further corroborated by fracture surface analysis which is shown in Fig. 11, where the micrographs after the 1st and 7th processing cycle are reported. A remarkable change in fracture surface morphology can be detected moving from the first to the seventh cycle. Indeed, the good interface between the fibers and the matrix ensured by the maleic anhydride grafted PP coupling agent and the higher length of the fibers after the first processing cycle lead to a brittle fracture. The full exploitation of basalt fibers induces a reinforcement dominated response as proved by the smoother fracture surface. Focusing on the composites after seven cycles, a more ductile behavior of the matrix can be observed with evident fibrillation signs. The reduction in fibers length leads not only to a decrease in composites stiffness which makes the matrix more prone to plastic deformation, but is also responsible for an ineffectiveness of the reinforcement. Indeed, the polymeric matrix displays a massive plastic deformation which develops around the short fibers, fully bypassing them.

By comparing the results obtained in the present work with other literature works, some important conclusions can be drawn. Many studies tried to develop bio-based composites with a PP matrix and vegetable fibers to ensure a partial biodegradability of the composite at the end of its life cycle and most works focused on flax fibers which are the most performing from a mechanical perspective. PP composites reinforced with 30 wt% of flax fibers and compatibilized with maleic anhydride grafted PP, i.e., the same conditions in terms of fibers weight percentage and compatibilization strategy used in the present work, displayed average values of tensile modulus between 2 and 2.7 GPa and of tensile strength between 25 and 40 MPa [23,40–42]. These values are perfectly comparable with the 3.5 GPa tensile modulus and 38 MPa tensile strength of the PP/basalt composites at the fifth reprocessing cycle reported in the present work. In a circular economy perspective, these results are really encouraging considering that PP/basalt composites can be conveniently exploited up to five times by repurposing

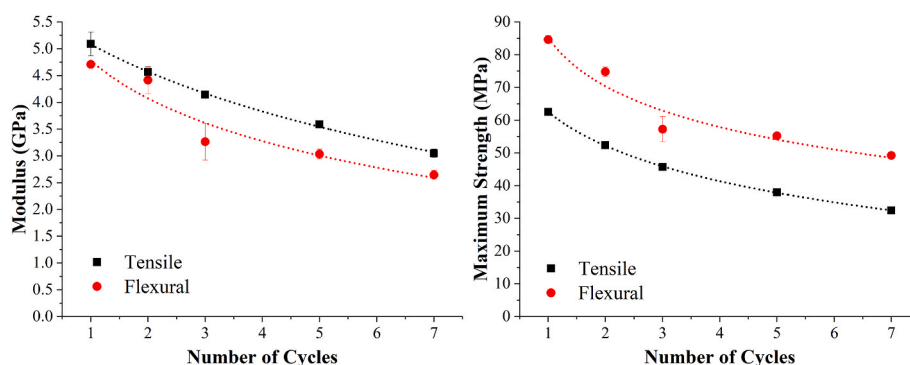


Fig. 8. Evolution of the tensile and flexural moduli and of tensile and flexural strengths as a function of the number of reprocessing cycles.

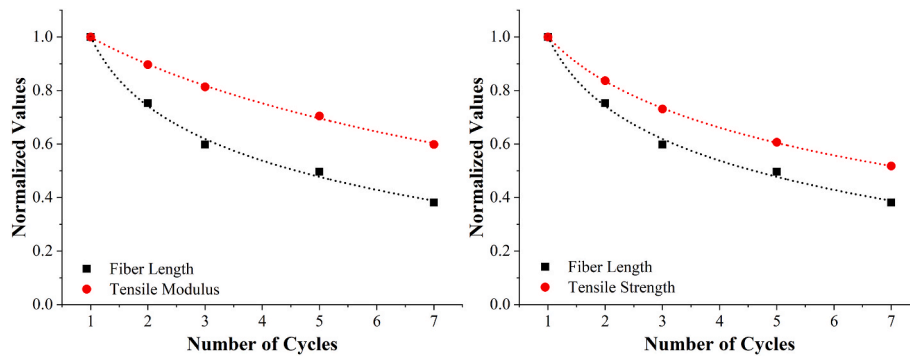


Fig. 9. Normalized values of PP/basalt composites fibers length, tensile modulus and strength as a function of the number of reprocessing cycles.

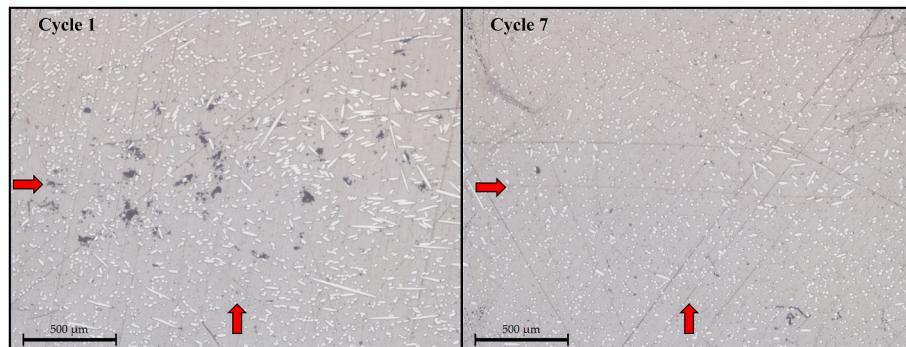


Fig. 10. Optical microscope micrographs of PP/basalt composites at the 1st and 7th reprocessing cycles which highlight fibers orientation with respect to the injection molding direction (red arrows highlight the direction from the mold surface to the inner parts of the specimen).

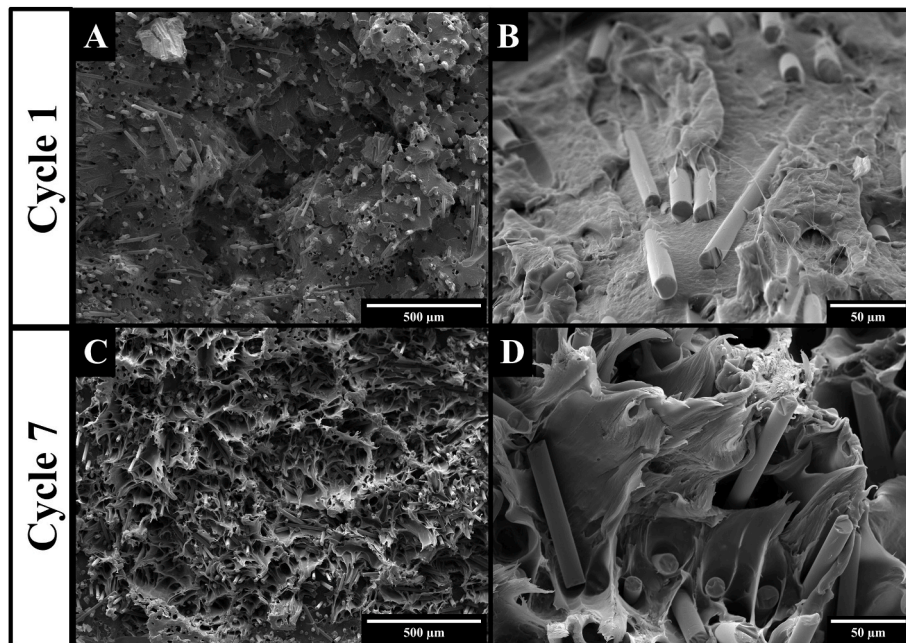


Fig. 11. Fracture surfaces of PP/basalt composites at the 1st and 7th reprocessing cycle at low magnifications [A,C] which display the overall morphology and at high magnification [B,D] which highlight the different interaction between the fibers and the matrix.

their final application rather than producing new PP/flax composites.

This path appears advantageous even from the manufacturing perspective, because the higher density of basalt fibers, i.e., 2.7–2.8 g/cm³ against the 1.4–1.5 g/cm³ of flax, entails a lower fiber volume fraction being equal the fiber weight fraction which in turn results in a

lower viscosity of the melt and an easier processability. This is confirmed by the data reported by Sojoudiasli et al. [43] and by Le Moigne et al. [44] who found a complex viscosity at an angular frequency of 1 rad/s higher than 10⁴ Pa × s for 30 wt% flax/PP composites which is more than one order of magnitude higher than the one observed

for PP/basalt composites in the present work. Similarly, Sergi et al. [23] reported an MVR value of $3.22 \text{ cm}^3/10 \text{ min}$ for 30 wt% flax/PP composites which is significantly lower than the $29.40 \text{ cm}^3/10 \text{ min}$ observed in the present work for basalt composites.

3.7. Charpy impact tests

Finally, the impact behavior of PP/basalt composites as a function of the number of reprocessing cycles and temperature was assessed through Charpy impact tests and the results obtained are summarized in Fig. 12.

Concerning the effect of temperature, a significant decrease in impact strength was observed moving from $+50^\circ\text{C}$ to -50°C for all reprocessing cycles. In particular, a decrease of 57 % was observed after the first reprocessing, of 66.6 % after the second reprocessing, of 70.9 % after the third reprocessing, of 64.5 % after the fifth reprocessing, and of 20.4 % after the seventh reprocessing. Analogous results can be detected comparing the cryogenic condition with room temperature one where a reduction of 30.3 % was observed after the first reprocessing, of 62.4 % after the second reprocessing, of 46.6 % after the third reprocessing, of 40.1 % after the fifth reprocessing, and of 18.9 % after the seventh reprocessing. This must be clearly ascribed to the overcoming of matrix glass transition temperature which ranges between -30.4 and -33.1°C , as shown in section 3.4, and causes a modification in polypropylene mechanical response from a glassy and brittle one to a more ductile and visco-elastic one. Concerning the effect of reprocessing cycles, a decrease in impact strength for increasing number of cycles was detected for all temperatures due to the progressive reduction in basalt fibers length which directly decreases the amount of energy dissipated by fibers pull out.

All these outcomes are confirmed by the analysis of the fracture surfaces and some representative micrographs, i.e., at the first and seventh cycles and at -50 and $+50^\circ\text{C}$, are shown in Fig. 13. Matrix embrittlement at -50°C deriving from PP glassy state can be easily recognized at both first and seventh reprocessing cycles as demonstrated by the smooth fracture surface. The cleavage plane can be identified clearly and univocally. On the contrary, the specimens tested at $+50^\circ\text{C}$ display a rougher surface with evident signs of matrix plasticization which endows the composite with a higher energy dissipation capability.

Significant differences in fracture surface can be also observed in terms of number of reprocessing cycles. Indeed, the PP matrix is strongly

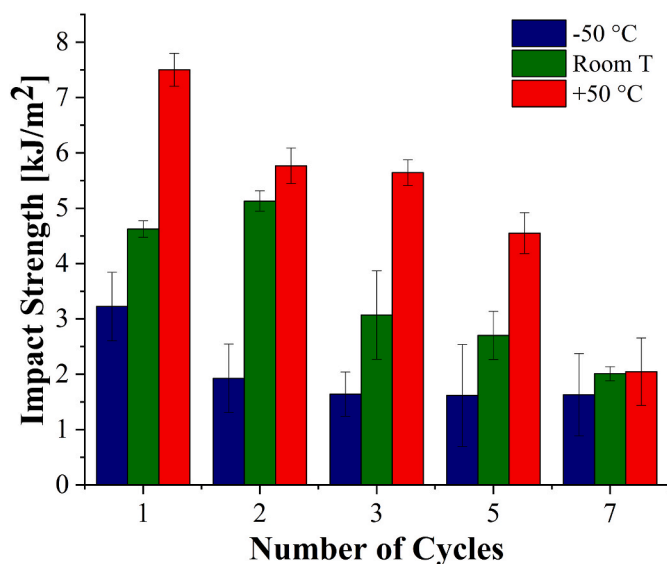


Fig. 12. PP/basalt composites Charpy impact strength as a function of the number of reprocessing cycles and of temperature.

bound to the base of the long basalt fibers which have been pulled out thus highlighting a good interface at both -50°C and $+50^\circ\text{C}$ after the first reprocessing cycle. On the contrary, at the seventh cycle only short fibers protrude from the surface highlighting a decrease in the fiber/matrix interface which was actively involved in energy dissipation.

4. Conclusions

Considering thermoplastic composites end-of-life, mechanical recycling is the recycling path characterized by the lowest environmental impact when compared with chemical and thermal recycling. Despite this, it exerts a significant detrimental effect on SFRPCs mechanical performance due to the strong decrease in length experienced by the fibers. In light of this and considering the progressive spread of basalt fibers on the market as a bio-based alternative to glass fibers, the present work focused on the mechanical reprocessing of PP/basalt composites up to seven cycles disclosing its effect on their thermal, rheological and mechanical properties and pointing out the main relationships which exist between fibers length and composites properties.

No significant variations were observed in composites for increasing reprocessing cycles in terms of degradation, glass transition, melting and crystallization temperatures as well as for crystalline structure and the degree of crystallinity.

Different is the situation for composites rheological behavior which is significantly affected by mechanical reprocessing. PP/basalt composites displayed a parabolic increase in MVR values for increasing reprocessing as a consequence of the combined effect of matrix molecular weight decrease and fibers length reduction. Moreover, they exhibited a lower MVR value than the neat matrix only up to the third reprocessing after which a switch in trend was observed due to a stronger degradation in polypropylene molecular weight resulting from the intimate contact with the basalt fibers and the related friction phenomena. These results were further corroborated by complex viscosity analysis.

Finally, with regard to the effect of fibers length reduction on composites mechanical properties, a non-direct proportionality was found between the decrease in normalized stiffness and strength values and the one experienced by the normalized values of fibers length. In particular, both stiffness and strength are characterized by a more gradual decrease thanks to a better orientation of the fibers along the injection, i.e., tensile, direction which allows to partially counterbalance their reduction in length.

Finally, the comparison of the mechanical results obtained in the present work with the data available for bio-based composites with a PP matrix and vegetable fibers allowed to conclude that PP/basalt composites are competitive with this type of composites up to the fifth reprocessing cycle. This might reduce the environmental impact of all the steps connected with vegetable fibers harvesting, transportation and extraction, but it is also advantageous in terms of processing conditions. Indeed, the use of basalt fibers entails a lower fiber volume fraction being equal the fiber weight fraction which in turn allows a lower viscosity of the melt, resulting in easier processability and potential reduction in the energy consumption.

CRediT authorship contribution statement

Claudia Sergi: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Luigi Botta:** Writing – review & editing, Methodology, Investigation. **Jacopo Tirillò:** Writing – review & editing, Validation, Supervision, Conceptualization. **Fabrizio Sarasini:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

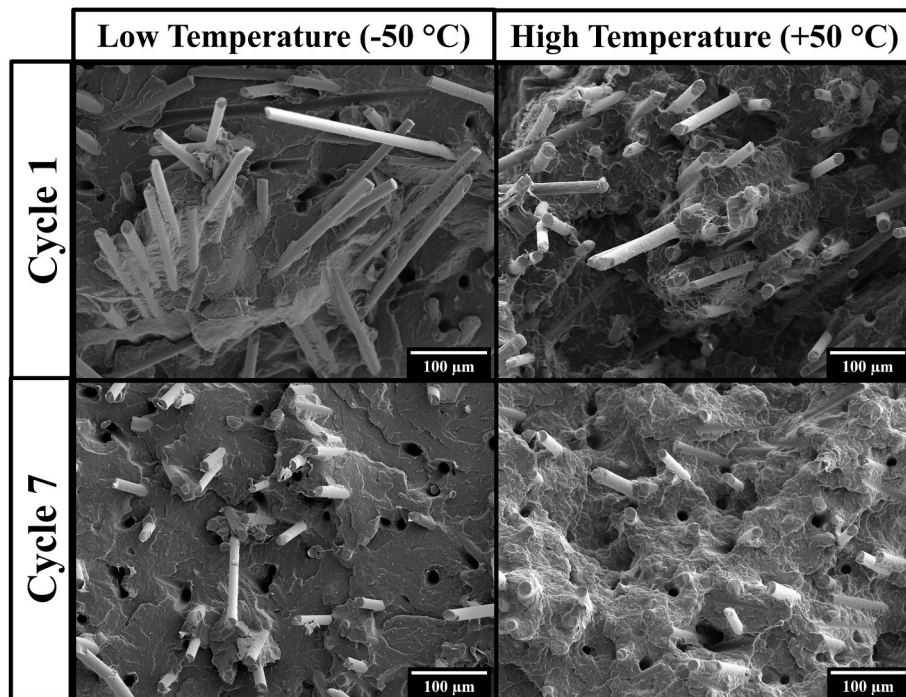


Fig. 13. PP/basalt composites fracture surfaces after Charpy impact tests at -50 and $+50$ °C and at the 1st and 7th reprocessing cycle.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data are contained within the article

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