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Valorization of basalt and glass fibres from vacuum infused acrylate-based composites by coupling mechanical and dissolution recycling pathways

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ABSTRACT

This work aims to couple two recycling pathways, i.e., a conventional mechanical recycling by grinding/sieving and resin dissolution in the case of vacuum infused Elium©/glass fabrics or Elium©/basalt fabrics composites. Quasi-static (tensile and bending) and dynamic (DMA) properties are evaluated on polyamide-6 (PA6) extruded specimens containing these recyclates, that underwent or not a dissolution in acetone. Commercial short glass and basalt fibres were used as a reference compared to waste products. Results show that the coupling allows to increase the fibre content in PA6 composites preserving a good interfacial adhesion, compared to a simple grinding process without dissolution. Tensile and flexural mechanical properties of the second-generation composites are increased. There is almost no variation in fibre length when comparing the reference, grinding alone and grinding/dissolved fibres. DMA allows to observe that in the case of short fibres within PA6, there is an increase of loss modulus especially.

1. Introduction

World production of plastics reaches 400 million tons per year including fibres, with an exponential growth of almost 9 % per year, leading to a doubling of production every 20 years. During their life cycle, plastics can end up in the environment, particularly in the aquatic environment [1]. The deposits of composites to be recycled are growing with approximately 20,000 t/year in 2021 and a forecast of 40,000 t/year in 2030. Most of the deposit comes from industrial waste (pre-consumer, production scraps, etc.). For example, end-of-life wastes from the wind and nautical industries will take an increasing share in the overall volume. By 2024, it is estimated that the composite waste stream for end-of-life boats could reach 4000 t/year (in France). The estimated mass of waste generated by wind power (wind turbine blades) worldwide by 2050 is 43 million tons [2]. These industries concern especially composites based on continuous fibres or fabrics. So, there is a necessary interest to implement recycling technologies for these ones.

1.1. Recycling technologies for fibre reinforced composites

Current recycling technologies for fibre composites are divided into mechanical, thermal and chemical methods.

Mechanical recycling involves reducing the size of composite waste into different size distributions of recycled material through sequential comminution processes. The first step in the mechanical recycling process is the grinding and micronization of composite parts into small fragments consisting of fibres and organic particles fractions of different particle size distribution more or less well separated. Then the powders and fibrous materials are separated, and the recycled product is used for new materials by reincorporation of these into thermosetting or thermoplastic polymers. To date, this mechanical method is considered as the industrial scale process available for recycling glass fibre reinforced polymers wastes [3]. This is a cost-effective process with a low environmental impact. But only short fibres and fillers can be recovered, albeit with lower mechanical properties for the fibrous fraction [4].

Other approaches, such as thermal and chemical recycling, allow the organic phase of the fibre to be separated by dissolution, depolymerization or pyrolysis of the polymer matrix. However, the energy consumption of these methods compared to the mechanical method makes them environmentally friendly only in the case of high-value material. According to Witik et al., pyrolysis of carbon fibre reinforced polymers requires 8,33 kWh/kg [5] although mechanical recycling by shredding of the same material requires 0,08 kWh/kg [6]. According to Fonte et al., recycling process cost of mechanical recycling is less than methods using

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pyrolysis or fluidized bed for example (89.39€/ton against 287.75€/ton considering electricity or 252.2€/ton considering gas). In addition, mechanical grinding enables to lower prices of recovered fibres. For example, shredded glass fibres have an estimated value ranging from 0.09 to 0.32 €/kg compared to glass fibres recovered with pyrolysis process (ranging from 0.54 to 0.87 €/kg) [7].

Compared to landfilling or incineration, mechanical recycling is an effective solution for glass and carbon reinforced polymers. For example, sheet molding compound (SMC) composites are converted to small sizes, i.e., SMC waste is granulated into fine powder by grinding. Then the fibre size is sorted using a pneumatic cascade classification. Palmer et al. used a zig-zag air-classifier and sorted coarse fibres to reprocess (28 %), useful coarse fibres (21 %), fine fibres (21 %) and powder (30 %) [8]. Sieving can also be processed by hydrocyclones, shaking screens [9] or pulverization where reduced sized recyclates are used as fillers for SMC. According to the size of the grid used, applied times of sieving, length of recovered fibres varies from hundreds of micrometers to many millimeters. In general, the replacement of 5 wt% to 30 wt% of virgin fibres with recycled fibres is recommended for the manufacture of composites to obtain optimal mechanical properties [10]. Kouparitsas et al. investigated the mechanical recycling of epoxy/carbon, epoxy/aramid and polyester/glass composites. Ground fibres have an average length of 6 to 8 mm and are reintegrated to thermoplastics such as polypropylene (glass fibre fraction of 12 % in volume) or ionomer (carbon or aramid fibre fraction of 9.6 or 9.0 % in volume respectively). A comparison of tensile properties of thermoplastic reinforced by ground fibres and virgin fibres shows similar tensile strengths and elastic moduli except for carbon/ionomer [11].

Shuaib et al. investigated the effect of comminution process parameters on energy consumption and associated recycling quality in the case of matter valorization of thermosetting-based glass fibre reinforced composites. The total energy demand of the mill is dominated by its base energy (required power). A machine with lower capacity is more energy efficient at a low processing rate while larger machines are better at higher processing rates [12]. The total energy depends on the size of the mill grid. A small grid size increases the residence time of the material in the mill chamber, which increases the energy demand. The thickness of the material also determines the energy requirements and cutting efficiency of the material. Thicker materials allow a more efficient cutting and a higher fraction of fine and cleaned recyclates. The design or choice of grinder grid is therefore an important factor in optimizing the quality of the recycled product. Finally, the thickness of the composite plate should be close to the air-gap, that is to say the free space between rotor and stator of the machine, to ensure an efficient cutting process [12].

On a general point of view, chemical recycling allows to recover continuous fibres with high strength retention and monomers can be recovered. Chemical recycling is often associated only to solvolysis, which is defined by the capability of the solvent to break the macromolecular chains. But dissolution can be also associated to chemical recycling. It corresponds to the disentanglement of the chains thanks to solvation. There is no breaking of macromolecular chains unlike solvolysis. This technique offers therefore many possibilities with a wide range of solvents, temperatures, pressures, and catalysts. In 2014, Arkema Co. introduced a new thermoplastic and recyclable resin, under the trademark Elium©150 resin. It is obtained from a low viscosity reactive mixture of polymer solutions of methacrylic monomers (methyl methacrylate (MMA), alkyl acrylic) and acrylic copolymer chains (viscosity of 100 cPs) and possibly other comonomers. It is a virtuous replacement for thermosetting resins as it remains thermoplastic but can be used as a thermosetting resin due to its low viscosity. Other studies have investigated respectively the dissolution process of acrylate-based composites [13] and solvolysis process ([14,15]). To our knowledge, there is no, work dealing with Elium©-based composites and combining material recovery by mechanical and chemical recycling. However, Perrin et al., proposed a treatment of SMC waste based on a grinding followed by a dissolution approach to recover long fibres and a high

fibre content (about 40 %wt). An initial shredding step with a slight crushing (from 2 to 10 mm of average length) is followed by a selective dissolution of calcium carbonate in an acid bath. In this study, dissolution increases the fibre fraction of the recyclate from 25 wt% to 41 wt%. Thanks to a 5 L-buffered orthophosphoric acid solution bath with a concentration of 0.3 mol/L, almost 50 % of the CaCO₃ is dissolved [16].

1.2. Valorization of recycled fibres

One way to recover recycled materials is to integrate them into new materials, particularly in a thermoplastic matrix such as polyamide 6 (PA6) or polypropylene (PP). Indeed, the PA-6-based thermoplastic polymers has become a popular matrix due to its good thermal stability, low dielectric constant and high tensile strength.

Regarding the focus on reinforcing materials in thermoplastic-based composites, the use of short fibres is increasingly operated in the plastics industry due to their good strength and durability. In particular, they are widely used in many areas such as aeronautics, aerospace or the automotive industry. In the automotive sector, fibre reinforced polymer composites are used for structural or semi-structural applications of components such as radiators, door beams, drive shafts and tanks.

Kiss et al. have studied the mechanical recycling of PP-glass fibre and PA6-carbon fibre composites (sandwich panels, SMC and monoliths). Reintegration of the recycled material into a thermoplastic reduces tensile properties, notably tensile strength, and Young's modulus, by up to 50 %. This is due to the loss of adhesion between the recycled fibres and the matrix. [17]

Otheguy et al. proposed mechanical recycling of commingled glass/PP (60/40 wt%) with balsa core material and paint, a waste from boats. They incorporated 5 recycled material batches containing various rates of PP, glass, and balsa into a virgin PP. They found out lower strength values than those of 1 mm fibre molding materials comparable with those of commonly short glass fibres reinforced PP composites [18].

The aim of this work is, on the one hand, to study the potential of recycling of Elium©/ glass or basalt fabrics composites by coupling mechanical and chemical recycling techniques. On the other hand, short fibres obtained from mechanical recycling are reintroduced in PA6 matrix and the mechanical properties of that PA6-based composites are studied. The purpose of dissolving the shreds in that case is to increase the fibre content in the second-generation composites. A comparison of the mechanical and thermomechanical properties as well as the matrix-fibre interface quality, with and without chemical dissolution is carried out. Reference composites based on commercial short glass or basalt fibres incorporated in polyamide-6 are used.

2. Materials and methods

2.1. Preparation of vacuum infused thermoplastic composites (1st generation composites)

Plain basalt fabrics (220 g/m², sizing suitable for epoxy, diameter 13 µm) provided by Basaltex (Belgium) and plain glass fabrics (202 g/m², sizing suitable for epoxy, diameter 13 µm) (provided by M.C. Technics (Belgium)) were used as reinforcements. A thermoplastic resin based on methacrylate provided by Arkema Co. (France) under the trademark Elium©150. 2 wt% of dibenzoyl peroxide (Perkadox© CH50X) was used as curing agent. Ten plies of fabrics are vacuum infused at 30 °C. The final material has a thickness between 1.5 and 2.0 mm. Glass and basalt composites have a fibre weight fraction of 71 %. Once the resin has polymerized the assembly can be removed after 24 h.

2.2. Mechanical recycling and dissolution conditions of 1st generation composites

Prepared basalt and glass reinforced composites are then roughly cut (3 × 2 cmxcm) with a circular saw and ground in a Retsch© SM 300

knife mill. An 8 mm grid is used at a speed of 1500 rpm. Then, in the case of glass reinforced composites, they were sieved for 30 min with 3 sieve sizes (6, 4 and 2 mm) after grinding. Basalt fibres have a cotton-like aspect implying that they cannot undergo a sieving process. Finally, only the fibre fraction higher than 2 mm is used. After passing through the mill and sieving, if necessary (in the case of glass), the fibre content is measured by calcination. This is $74.06 \pm 0.36 \%$ in the case of the Elium©150/ground basalt, but lower in the case of the Elium© 150/glass after the grinding and sieving step ($60.98 \pm 0.27 \%$). Thus, the residual resin content is lower in the case of basalt.

Resulting ground (and sieved for glass-based composites) materials were dissolved according to a protocol that were deeply optimized and described in detail in a previous paper [13]. They were dissolved in chemical SLR Fisher acetone (99.9 % purity) in a ratio of 1:20 for 16 h with 3 min of ultrasound at the beginning of the dissolution process. A metallic grid in a 800 ml beaker was used to contain the ground (and sieved) material during the dissolution.

It can be noted that in a previous study [13], the potentiality for the Elium© resin to be recovered has been carried on. Fourier transform infrared spectroscopy (FTIR) analyses and gel permeation chromatography (GPC) measurements showed that Elium© was fully (over 90 %) recovered with a combination of degradation of long chains and their recombination [19].

2.3. Processing of 2nd generation composites based on polyamide-6 and shredded fraction obtained after mechanical and dissolution recycling pathways

The shredded fractions were reincorporated in a thermoplastic matrix to evaluate the mechanical properties of these 2nd generation composites. Semi-crystalline polyamide 6 (PA6) Akulon© F223—D (DSM Engineering Materials, Belgium) was used due to its widespread use in the automotive industry. New compounds are manufactured by extrusion of shredded fractions and PA6 into a co-rotating twin-screw extruder (Clextral BC 21, L/D = 43) loaded at 20 wt%. Extrusion temperature was 240 °C. A comparison with reference compounds made from virgin short glass fibres (4.5 mm length, 10 mm diameter; sizing suitable for polyamides; OCV, France) called refG and short basalt fibres (3.2 mm length, 13 mm diameter; sizing suitable for polyesters; Basaltex, Belgium) named refB was also carried out. The dumbbell test pieces (ISO 1A) were produced after a suitable drying of the compounds at 80 °C for 24 h, by injection in a 50 t Krauss Maffei press. Temperature for injection was 220 °C.

Dumbbell test pieces were named as following: refB for Reference short Basalt fibres, refG for Reference short Glass fibres, GB for Ground Basalt fibres, G/S G for Ground Glass fibres (fraction >2 mm), G/D B for Ground and Dissolved Basalt fibres and G/S/D G for Ground, Sieved and Dissolved Glass fibres (fraction >2 mm).

A schematic diagram of the recycling process coupling mechanical and chemical method is presented on Fig. 1. The above sample nomenclatures are indicated on this figure.

2.4. Loss of ignition test

Loss on ignition tests were performed to determine either the fibre content of PA6 based composites or the residual resin content within shredded composites. The tests were carried out according to the NF EN ISO 1172 standard. About 2 g of samples are placed in a ceramic crucible and calcinated at 600 °C for 1 h. Each sample were tested in triplicate.

The fibre weight content of PA6 based composites is calculated according to the following equation:

$$W_f = \frac{mf}{mc} \times 100 = \frac{\text{mass composite after test}}{\text{mass composite before test}} \times 100 \quad (1)$$

Where W_f (%) is weight percentage of fibre, mf (g) is the mass of fibres and mc (g) is the mass of composite.

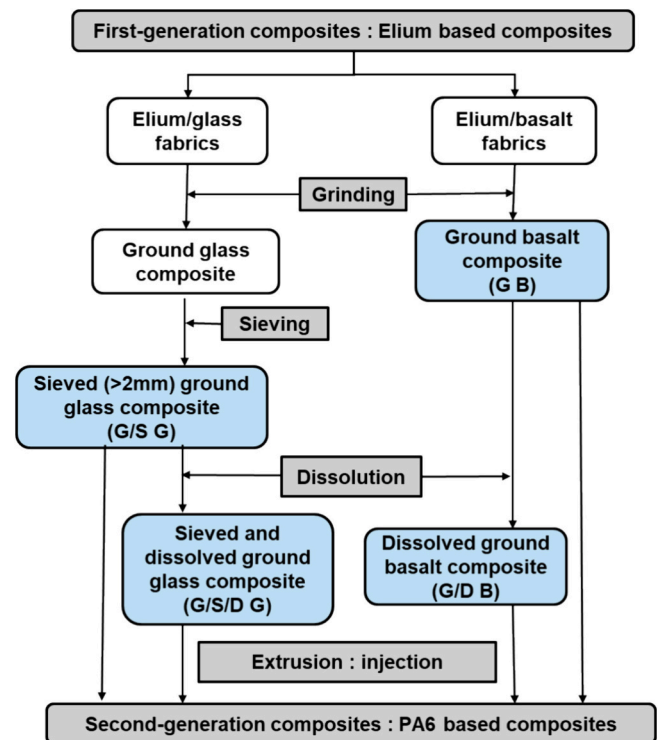


Fig. 1. Schematic diagram of the recycling process coupling mechanical and chemical method.

The percentage of residual resin within shredded composites is defined as the rate of resin present on the fibres resulting from the dissolution, noted %RR. It was calculated with the following formula (eq. 2):

$$\%RR = \frac{\text{mass of fibres before test} - \text{mass of fibres after test}}{\text{mass of initial composite}} \times 100 \quad (2)$$

2.5. Pycnometry

Pycnometry analysis were carried out to measure the fibre volume fractions within the PA6 second-generation composites (2 or 3 rectangles of composites for each measure, Micrometrics AccuPyc 1330, Verneuil en Halatte, France).

2.6. Mechanical performance by quasi-static uniaxial tensile test

The specimens were tested by uniaxial tensile tests according to standard (ISO 527) on a Zwick Roell Z010 press with a 10 kN force sensor and strain-gage contact extensometer, with a speed of 1 mm/min. The 3-point-bending tests were performed according to ISO 178 using a crosshead speed of 2 mm/min.

2.7. Microstructural observations by ESEM

Environmental scanning electron microscope ESEM on FEI QUANTA 200 FEG observations are used to observe the fracture surfaces of dumbbell test pieces after tension strength tests. These also allow observing the interfacial adhesion between recycled fibres and PA6.

2.8. Macromolecular characterization by DSC

Differential scanning calorimetry DSC on Perkin Elmer instruments with the software PYRIS Diamond DSC to look at the fibre/matrix

interface and crystallinity respectively.

Melting temperature (T_m), heat of fusion (ΔH_f) and the relative degree of crystallinity (X_c) values of the PA6 based composites were measured by differential scanning calorimeter analysis (DSC) (Perkin) under nitrogen. The DSC analysis was carried out in the temperature range from 30 °C to 300 °C at a heating rate of 10 °C/min. The relative degree of crystallinity was calculated with the following expression (eq. 3):

$$X_c = \frac{\Delta H_m}{\Delta H^* m \cdot (1 - f)} \quad (3)$$

Where $\Delta H^* m$ is the fusion enthalpy of 100 % crystalline PA6 (190 J/g) [20] and f is the fibre fraction in the composite.

2.9. Dynamic mechanical analysis (DMA)

Dynamic Mechanical Analysis (DMA) was used to determine the thermomechanical properties and damping of a material according to the standard ASTM D5026. Analyses were performed on PA6 composite samples (dimensions 10 × 50 × 4 mm³) in triplicate from room temperature up to 180 °C at a constant frequency of 1 Hz and a dynamic displacement of 10⁻⁶ μm (DMA 50 N O1-dB, France). First, linearity tests and a frequency sweep between 0.1 and 100 Hz at room temperature were carried out to verify the viscoelastic properties of the material and select the right dynamic displacement.

2.10. Fibre length measurement by optical microscope observations

Fibre length within PA6 based composites and within shredded composites before their incorporation in PA6 were determined. Samples were first calcinated at 600 °C during 1 h. Around 40 mg of residual fibres were diluted into 200 ml of distilled water in an Erlenmeyer. Manual agitation is required to disperse the fibres efficiently. A Büchner setup was used to filter the fibre solution while dispersing the fibres on a microscope plate. Microscope plates were then observed using a Leitz optical microscope in transmission mode. Pictures were treated with ImageJ© software. Fibre length distributions were obtained thanks to ct Fire© software.

3. Results and discussion

3.1. Characterization for shredded composites

Figure 2 shows the influence of the grid size with 3 grid sizes (4, 6, 8 mm), at the same speed of 1500 rpm, on fibre weight fractions of Elium©/glass ground composites.

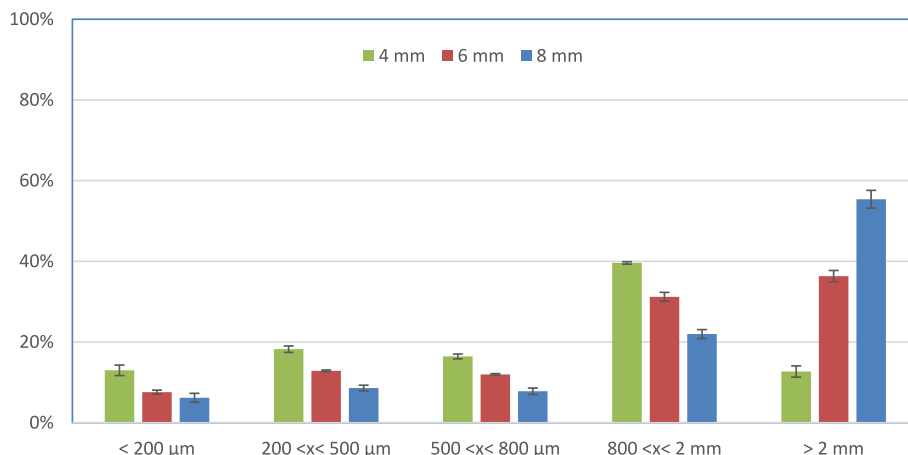


Fig. 2. Weight fractions of Elium©/glass ground composites with 3 grid sizes (4, 6, 8 mm, at the same speed of 1500 rpm).

Results show that the size of the grid allows an enrichment of the small fractions (those <800 μm) at the expense of the large ones. This enrichment occurs progressively. The trend changes up to 800 μm here greater grid size allows more composite chips to pass through. The standard deviations do not overlap. Thus, the percentage of crushed material in the fraction greater than 2 mm drops from 55 % to 36 % and then 12 %, i.e., 80 % less than for the 8 mm grid. This decrease is not as marked for the other fractions, but a difference of 5–10 % can be observed for each fraction.

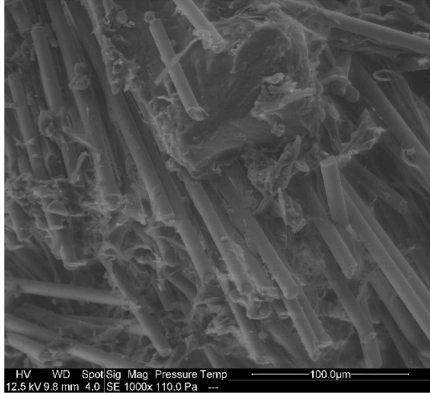
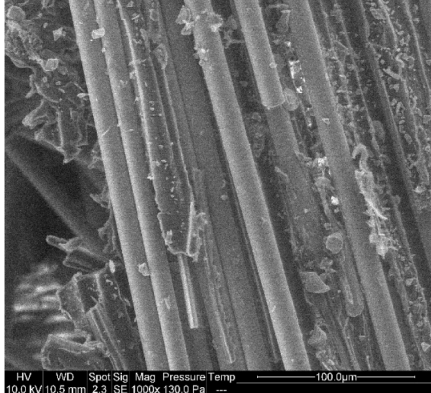
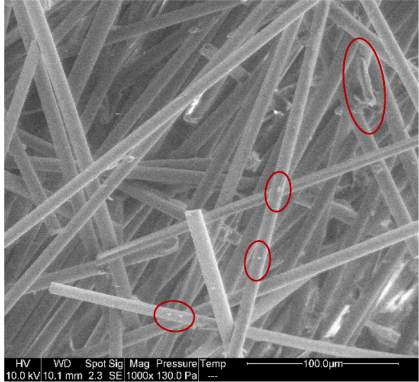
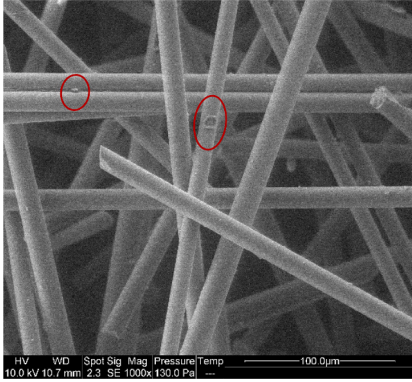
For this study, the choice of the grid must be oriented towards the one that allows obtaining a larger fraction of one or more granulometric classes that will be subsequently reincorporated. However, the energy cost is also to be considered. However, since fibre size is a determining factor for the mechanical properties of composites, it must also be optimized. Indeed, a thin grid makes the passage of the fibres more difficult. The attrition, the degradation of these last ones would then be more important than with a larger grid.

These data give evidence that the size of the grid plays a significant role on the distribution of the different particle size fractions. However, the choice of the grid was extended to that of 8 mm in view of the recovery rate of the crushed material greater than 2 mm, which is important and recommended for a final optimized fibre length in PA6 composites.

The SEM resulting fractions as well as their weight content of fibres are shown in Table 1. SEM images show clear differences between ground, ground/dissolved and ground/sieved/dissolved materials. Observations show that G B shredded composites show a fluffy appearance which prevents it from being sieved so that no peculiar fraction was chosen as it was the case for G/S G shredded composites. Moreover for both G/S G and G B shredded composites, it has been shown that the residual Elium© resin agglomerates the fibres and creates small solid packets, that are difficult to disperse. The residual resin content of ground/dissolved composites turns around 8 % (for both basalt and glass based composites) against 26 % (basalt composites) and 39 % (glass composites). The ultrasound process employed facilitates the dispersion of fibre in the solvent (acetone) to prevent resin agglomeration on fibres without affecting the morphology of the latter [13]. This technique was compared to simple mechanical stirring. Both techniques are efficient regarding dissolution, but ultrasounds prevent textile damaging. Finally it can be observed that much more resin is present on ground materials and fibres are plain-like agglomerated. Fibres are thus well aligned. After dissolution a major part of the Elium© resin is not yet present on the fibre surface (red circles in Table 1). The increase of fibre content after dissolution (+52 % and 25 % for glass and basalt fibres respectively) is observed.

Table 1

Weight fibre contents and SEM images of ground (G), ground/dissolved (G/D) and ground/sieved/dissolved (G/S/D) glass and basalt-based composites.

Glass		Basalt	
G/S G		G B	
			
Wf: 60.98 ± 0.27 wt%		Wf: 74.08 ± 0.36 wt%	
G/S/D G		G/D B	
			
Wf: 92.91 ± 2.25 wt%		Wf: 92.37 ± 2.41 wt%	

3.2. Mechanical properties of PA6 composites

Table 2 shows the influence of recycling conditions on the tensile properties of PA6 composites.

Regarding the maximum stress, whatever the fibre (glass or basalt), a decrease of 11 % (glass) to 15 % (basalt) is observed after grinding (basalt) and grinding and sieving (glass) compared to the reference. This drop is less marked after dissolution and is of the order of 10 %. This result is related to the lower fibre content (14 %) after grinding.

As regards Young's modulus, whatever the fibre, a decrease of 14 % was observed after grinding (basalt) and grinding and sieving (glass) compared to the reference. But after dissolution a higher tensile modulus (+15 %) is observed. This result is very interesting regarding the valorization potential of Elium®/glass and Elium®/basalt composites.

Table 2 shows the bending mechanical properties of the PA6 composites.

Regarding the strain stress at maximum strain, a grinding/solvolytic treatment decreases the strain at maximum strain by 3 % in the case of basalt and by 4 % in the case of glass compared to the reference. Grinding alone implies a decrease of 9 % and 3 % for basalt and glass-based composites respectively.

As far as Young's modulus is concerned, there is a decrease in flexural modulus in the case of grinding alone for basalt (−10 %) and glass (−7 %). However, the grinding/solvolytic coupling involves an increase of 7 % for basalt and 2 % for glass. This can be explained by a higher fibre volume fraction in the case of grinding/solvolytic than in the case of

grinding alone.

Flexural stresses are higher than tensile stresses, due to a different origin of fracture. Flexural fracture is caused by defects, such as fibre aggregation during extrusion. In addition, the specimen is less stressed than in tension.

3.3. Fibre length measurement

The mechanical properties of a composite containing short fibres depend on the efficiency of the load transfer between matrix and fibres. During damage mechanisms fibres are pulled out from the matrix before fibre failure, limiting the optimization of the strength of composites [21]. This means that a study of the fibre length is a need to better understand the mechanical properties of SFRTs.

Regarding the fibre diameter (Table 3), it appears that short basalt fibres have an average diameter of 13 µm compared to 9 µm for short glass fibres, which agrees with the initial diameter of the commercial fibres. The fibre length in fabrics is however the same for basalt and glass. Regarding the glass fibre diameter, this has no impact on tensile modulus although a higher fibre diameter decreases the tensile strength. In addition, the higher the glass fibre content the better the mechanical properties up to 40–50 %wt. [21–23]

The average fibre length is between 160 and 220 µm for all composites. In the case of basalt-based composites, a progressive increase in fibre length was observed between the reference fibres (175 ± 132 µm), the ground fibres (185 ± 138 µm) and the fibres ground and then

Table 2

Influence of the coupling of mechanical and chemical recycling on the tensile and flexural properties of PA6/glass and basalt composites.

PA6/fibres composites		Maximum stress (MPa)		Young's modulus (GPa)		Vf (%)
PA6/ Basalt	G/D B	109.5 ± 1.8	−10.2 %	7.2 ± 1.2	+16.3 %	13.58
	GB	103.6 ± 0.9	−15.1 %	5.4 ± 0.4	−13.4 %	9.21
	ref B	122.0 ± 2.9		6.2 ± 0.1		13.60
	G/S/D	108.3 ± 4.6	−9.6 %	7.0 ± 1.6	+14.7 %	9.81
PA6/ Glass	G	106.8 ± 0.7	−10.8 %	5.3 ± 0.2	−14.2 %	6.68
	G/S G	119.7 ± 1.9		6.1 ± 0.2		9.93
	ref G					
	G/S/D					
PA6/fibres composites		Deformation stress at elastic deformation (MPa)		Bending modulus (GPa)		Vf (%)
PA6/ Basalt	G/D B	159.17 ± 4.21	−2.5 %	5.22 ± 0.09	+6.5 %	13.58
	G B	149.12 ± 1.74	−8.6 %	4.42 ± 0.20	−9.8 %	9.21
	ref B	163.13 ± 1.03		4.9 ± 0.06		13.60
	G/S/D	151.54 ± 0.99	−3.8 %	4.84 ± 0.09	+1.9 %	9.81
PA6/ Glass	G	154.26 ± 1.41	−2.5 %	4.65 ± 0.20	−6.3 %	6.68
	G/S G	157.73 ± 5.44		4.75 ± 0.23		9.93
	Ref G					
	G/S/D					

Table 3

Measured average fibre length and fibre width of fibres in PA6 composites.

	refB	GB	G/D B	refG	G/S G	G/S/D G
Average fibre length (µm)	175 ± 132	185 ± 138	203 ± 140	187 ± 60	212 ± 124	164 ± 136
Average fibre width (µm)	12 ± 3	12 ± 3	13 ± 3	9 ± 2	13 ± 2	12 ± 2
Shape factor	14.6	15.4	16.6	20.8	16.3	13.7

solvolyzed ($203 \pm 140 \mu\text{m}$). This increase is generally related to a poorer quality of fibre/matrix interface which results in lower melt shear stresses during extrusion. This result can be correlated with the decrease in the maximum tensile stress. In the case of glass-based composites, there is an increase in fibre length between the reference fibres ($187 \pm 60 \mu\text{m}$) and the grinded material ($212 \pm 124 \mu\text{m}$), indicating a poorer interface due to the presence of residual resin and correlating with the decrease in ultimate tensile stress. When a subsequent dissolution of the resin is carried out, a decrease in the length of the fibres ($164 \pm 136 \mu\text{m}$) is evidenced which can justify an improvement in the interfacial quality, in connection with the increase in modulus.

The shape factor of the fibres is also important. In this study, however, it remains almost constant at around 15, except for the reference PA6/glass composite (around 21), linked to the different fibre diameters.

Regarding mechanical properties, average length of fibres may not have an impact on flexural and tensile strength. Except for G/D B and G/S G, average fibre lengths are close. However, difference in morphology of fibre between reference and recycled materials must be considered. In fact, reference material is composed of short fibres although recycled materials is composed of ground fabrics. This is particularly true for glass as the obvious difference in shape factor shows.

3.4. Thermomechanical properties

Thermomechanical properties of PA6 are presented in Fig. 3.

In the case of glass and basalt-based composites, there is a decrease in the temperature of the main relaxation associated with the glass transition of PA6 of 12 % (i.e., from $65 \text{ }^\circ\text{C}$ to $57 \text{ }^\circ\text{C}$ for glass) and 10 % (i.e., from $70 \text{ }^\circ\text{C}$ to $61 \text{ }^\circ\text{C}$ for basalt) when recycled fibres are used. For the only one grinding step of fillers/PA6 composites, a relaxation peak near $115 \text{ }^\circ\text{C}$ can be observed and corresponds to the Elium©150 of the initial composite. [13]

As regards basalt-based composites, the grinding/solvolytic coupling has no effect on the damping peak width and intensity, whilst it is lower for glass-based composites.

As far as the storage modulus is concerned, in the case of basalt-based composites, it is close between the reference (refB) and the grinding/solvolytic coupling (G/D B), which is logical due to the similar weight fibre content (20 %). The storage modulus of ground fibre composite (G/B) is lower than both others due to lower fibre content (14 %). The loss modulus reaches a peak at around $50 \text{ }^\circ\text{C}$ for both reference (refB) and grinding/solvolytic coupling (G/D B), in the case of basalt. However, for ground fibre composites (G/B), maximum in the loss modulus may occur around ambient temperature. These evolutions agree with the differences in fibre contents.

In the case of glass, the storage modulus doubles between the reference (refG) and the grinding/solvolytic coupling (G/S/D G). Maximum peaks of loss moduli are close for reference, ground, and ground/dissolved material. Also, the ground/dissolved fibre composite dissipates a much higher amount of energy. There are more molecular rearrangements during the temperature increase and the deformation. Thus, the nature of the fibre implies a different thermomechanical behavior of PA6 composites.

3.5. SEM analysis

SEM was used to observe the fracture profiles of PA6 composites, especially the quality of the matrix-fibre interface. This has a particular influence on the ability to transfer stresses.

In the case of the reference basalt composite (refB), most of the fibres are not covered by the matrix after rupture, with the presence of holes corresponding to loosening, which indicates poor interfacial quality. This can be explained by the fact that the sizing of these basalt fibres is compatible with an epoxy resin and not with a polyamide matrix (Fig. 4a).

In the case of the reference glass composites (refG) (Fig. 4b) and the ground/sieved/dissolved glass composites (G/S/D G) (Fig. 4f) obtained from the Elium©/glass composites, the fibre/matrix adhesion appears to be good. Regarding refG, this may be due to the presence of a suitable sizing for the polyamide. In the case of G/S/D G, this may be related to the presence of residual Elium© resin on the fibre surface which adds both surface topography (mechanical adhesion) and modifies the surface properties of the fibres (physico-chemical wetting adhesion).

SEM images of G/S G composites (Fig. 4c) and GB composites show a lower quality interface than that of composites with solvolytic grits (G/S/D G for glass and G/D B for basalt). Some fibres are pulled out from the matrix, others are broken. Broken fibres have no resin on the surface. Fibres are agglomerated thanks to the presence of residual acrylate resin, and less dispersed in the ground material. The presence of particles is typical of poly methyl methacrylate acrylic (PMMA)-PA6 blends. PA6 which is crystalline and PMMA which is amorphous, are immiscible [24,25] thus PMMA appears like particles in PA6.

To explain worse mechanical properties for ground material compared to reference or ground/ dissolved material (apart from the fact that fibre volume fraction is lower for ground composites), Fig. 5 proposes a schematic interface for both ground and ground/dissolved material. The main explanation for ground material is the Elium©/PA6 immiscibility (Fig. 5 a)) [24,25] which could lower the initial PA6

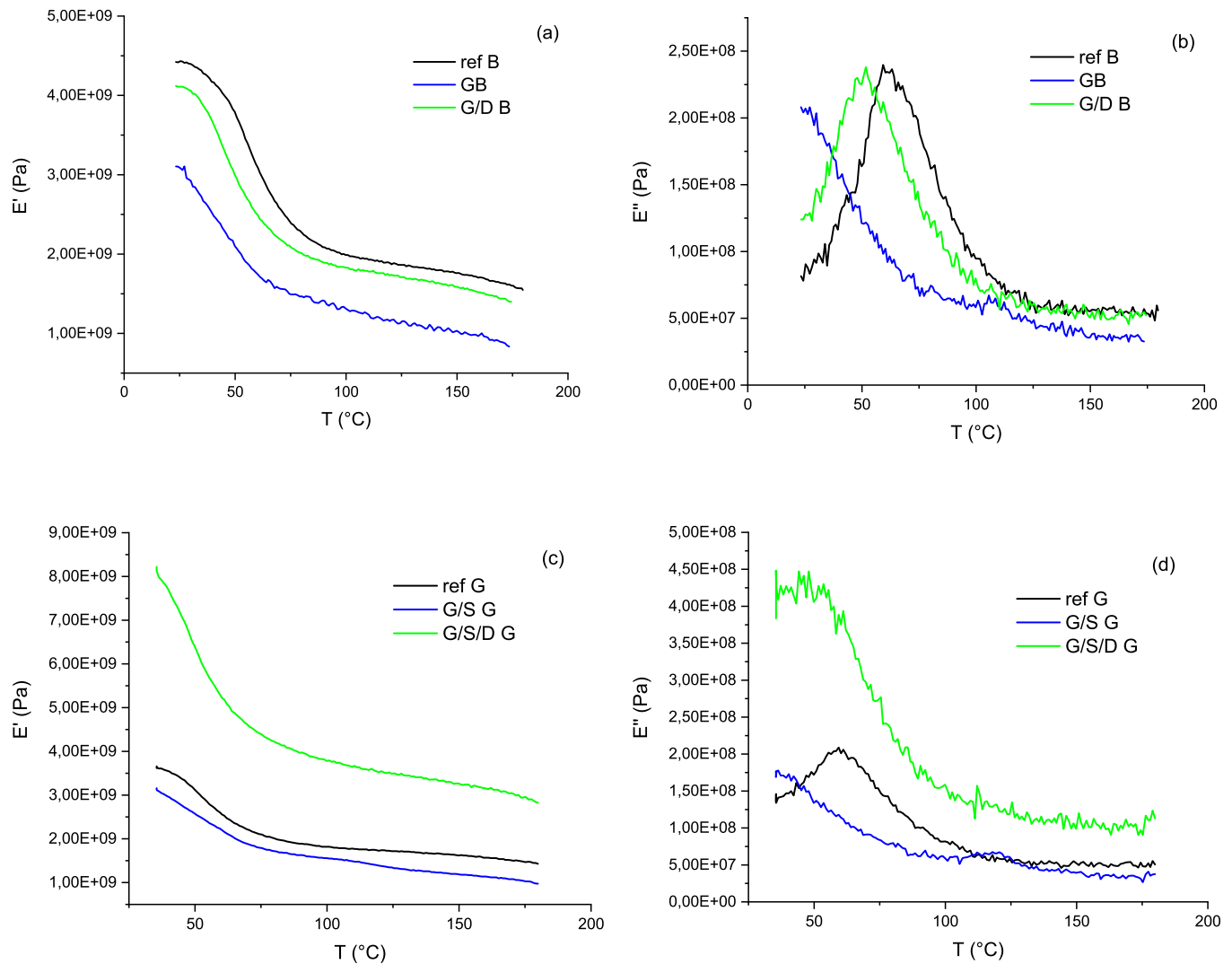


Fig. 3. Evolution of storage modulus E' (a), loss modulus E'' (b) for PA6/basalt fibres composites, storage modulus E' (c) and loss modulus E'' (d) for PA6/glass fibres composites.

tensile properties. In the case of ground/dissolved material, the residual resin content of Elium© is lower, thus a hypothesis is made. Fig. 5 b) considers a potential interaction between amine groups of polyamide-6 and acrylate functions of Elium© resin. These groups could interact by hydrogen bonding [26]. This is why no particles are observed in the matrix area (Fig. 4 e) and f)).

For deeper analysis of the mechanism, surface properties of ground and ground/dissolved materials should be envisaged. But a deeper Elium©/PA6 miscibility study could also be done, regarding rate of Elium© in PA6, through the elaboration of model blends. Also adding compatibilizing agents could be an interesting way to valorize ground materials without adding a dissolution step in the recycling process.

3.6. DSC analysis

The results (Table 4) show that PA6 has a melting temperature around 224 °C and the crystallinity ratio of 36 %. Melting temperatures of PA6 composites remain close to 225 °C, corresponding to PA6 melting temperature when standard deviation is considered. It can be noted a slight increase of the melting temperature for the refG composite that can be related to the presence of a sizing of the reference glass fibres more compatible with the polyamide matrix.

Furthermore, it is observed that the incorporation of fibres in PA6 decreases X_c from 36 % to 23–27 % depending on the composite. Indeed,

the fibre content influences the value of X_c since the fibres create nucleation sites. When comparing all composites, no significant variation is observed even though fibre contents are different and that there is 6 % residual Elium© resin mixed with PA6.

4. Conclusion

There is an interest in coupling both grinding and dissolution processes for the recycling of Elium©/glass or basalt fabrics composites. No studies have been reported in the literature on the subject.

One goal of dissolution was to increase the fibre content in the second-generation composite compared to a simple grinding. The fibre content is increased by 6 % thanks to dissolution. This implies better tensile properties. The maximum stresses reached for ground and ground/dissolved fibres composites decrease compared to the reference for glass and basalt. However, there is an increase in Young's moduli of 16.3 % for G/D basalt and of 14.7 % for G/S/D glass. Regarding flexural strength, the deformation stresses at elastic deformation of ground and ground/dissolved fibres composites are lower than the references for both glass and basalt. However, there is an increase of bending moduli of 6.5 % for G/D basalt composites and of 1.9 % for G/S/D glass composites. For basalt fibres, no sieving has been processed because of the cotton aspect, compared to glass.

Extrusion process implies limiting the average fibre length to around

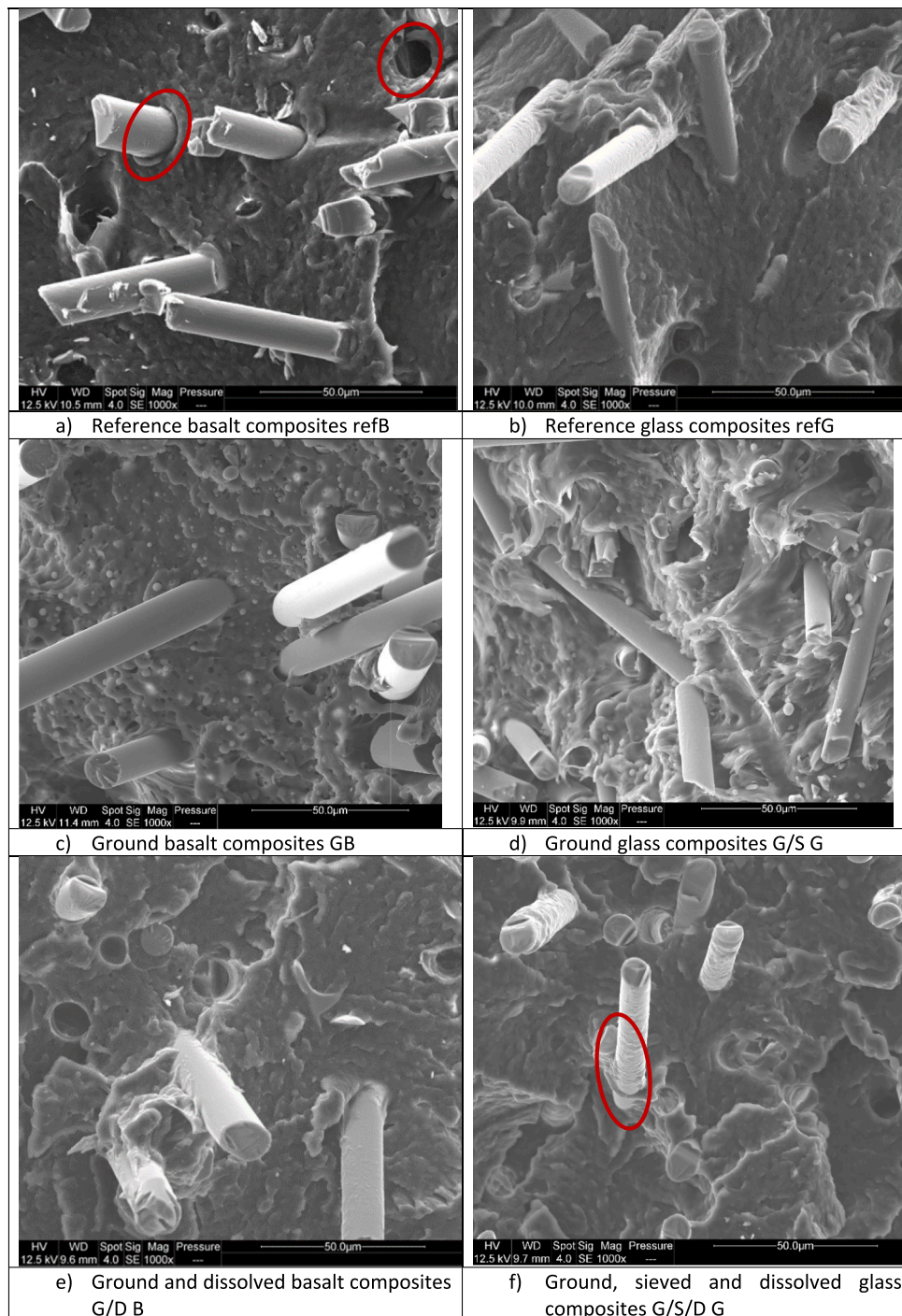


Fig. 4. Influence of the combination of mechanical and chemical recycling on the fracture profiles of PA6/basalt and PA6/glass composites observed by SEM - magnification x1000.

200 μm. Dissolution does not influence the fibre length of recycled fibres. SEM analysis showed a better matrix-fibre interface in the case of grinding/dissolution. This participates to improve Young's modulus of second-generation composites. So, the interest of adding a dissolution step to a grinding process has been shown from a mechanical point of view. The incorporation of recycled fibres in PA6 via extrusion does not influence the crystallinity of the polymer. So, there is a real advantage to add a dissolution step to grinding for reincorporation of recycled fibres into a thermoplastic matrix such as PA6.

Reincorporation of grinded and dissolved basalt or glass fibres into PA6 thermoplastic matrix is an interesting way to valorize end-of-life

plain thermoplastic composites.

CRediT authorship contribution statement

I. Meyer zu Reckendorf: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **A. Bergeret:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **D. Perrin:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **C. Lacoste:** Writing – review & editing, Validation,

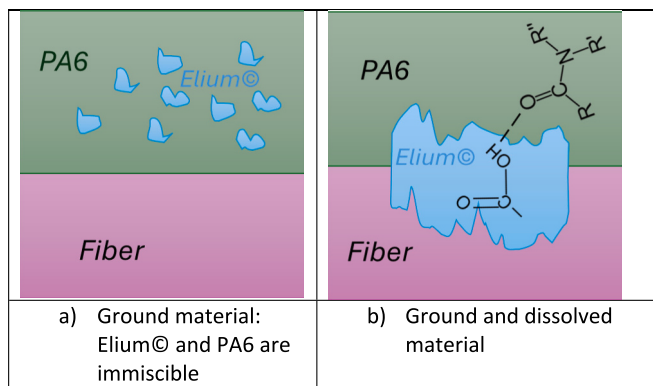


Fig. 5. Schematic interface of a) ground and b) ground/dissolved materials.

Table 4

Melting temperatures (T_m), and crystallinity ratio (X_c) for virgin PA6 and PA6 composites.

	Wf (%)	Residual Elium© (%)	T_m (°C)	X_c (%)
PA6	0	0	223.99 ± 0.41	35.91 ± 4.24
refG	20	0	228.31 ± 1.85	22.76 ± 1.93
G/S G	14	6	224.42 ± 0.67	25.01 ± 2.24
G/S/D G	20	0	225.86 ± 3.51	26.42 ± 1.67
refB	20	0	224.61 ± 0.58	27.14 ± 1.50
GB	14	6	225.38 ± 0.23	25.00 ± 1.66
G/D B	20	0	225.28 ± 0.80	27.22 ± 0.91

Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **K. Morand**: Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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