

# NOVEL MANUFACTURING PROCESS FOR NATURAL FIBRE COMPOSITES OUT OF BIOBASED AND BIODEGRADABLE MATERIALS

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## ABSTRACT

The use of natural fibres is an approach to address the issue of sustainability in the field of composites. With regard to potential recycling strategies for composites, natural fibres are particularly relevant in conjunction with biodegradable matrix materials. In addition to polysaccharides and lipids, proteins offer potential. Compared to conventional matrix materials such as epoxy resins, these kinds of natural materials cause some challenges in terms of processing. Combining two existing processes made it possible to produce flax fibre composites with a matrix based on the protein zein sourced from agricultural industry residues. A pre-impregnation of the flax fibres with the matrix ensures adequate infiltration of the flax fibres. By alternating stacking with films of the same matrix material, a good fibre-matrix bonding could be achieved, as shown with transverse tensile tests. By further modifying the matrix material, the mechanical properties were significantly improved.

The developed manufacturing technique allows the reproducible fabrication of laminates with high quality. Therefore, unidirectional and cross-ply [0/90]<sub>2s</sub> flax fibre biocomposites were manufactured and characterised in terms of mechanical performance and optical damage analysis. While the unidirectional specific tensile strength of the novel biocomposites with protein-based matrix already reaches approx. 80 % of the best epoxy-based flax fibre composites available on the market, the achieved stiffness is already on the same level. Consequently, a comparison with other “green composites” highlights the competitiveness of fully biodegradable materials. The major advantage of the presented biocomposites, which makes them superior to all others in terms of sustainability, is the degradation by biological activity demonstrated in home composting. Recycling is thus possible even in the simplest conceivable process. Industrial composting at elevated temperatures and shredding of the composites can additionally lead to faster decomposition rates.

## 1 INTRODUCTION

These days, climate change is a major challenge for our society. Topics like microplastics in the marine environment and the recycling of plastics and composites are highly debated. One way to deal with this challenge in terms of composites is the use of biobased and biodegradable materials. Compared to glass fibres, natural fibres such as flax often offer competitive specific properties due to their low densities and can thus contribute positively, e.g., to reduce fuel consumption in the mobility sector. In addition, natural fibres offer the advantage of positively influencing the carbon footprint through CO<sub>2</sub> absorption during growth [1]. Up to now, natural fibre composites have mainly been used industrially with petrochemical matrices, especially with thermosets. This leads to well-known problems regarding climate-neutral recycling. For example, the Porsche AG uses natural fibre composites with an epoxy resin matrix for car body kits [2].

The use of biodegradable matrix systems offers a solution to the challenge of recycling, but so far, the mechanical properties are much lower than for conventional thermosets [3]. Furthermore, the negative aspects of natural materials must be considered too. These include the dependence of quality on climatic conditions and the competition for cultivation space with food industries. However, conventional methods cannot necessarily be used, so new processes must be developed.

## 2 MATERIALS

Biobased composites were manufactured with unidirectional flax fibre fabric ampliTex™ 5009 (300 g/m<sup>2</sup>) delivered from BComp Ltd (Fribourg, Switzerland). Zein is used as biobased and biodegradable matrix material. The protein-based material (REF1) is modified to 20 wt.-% with an additive mix of two processing additives (P1, P2) and a hydrophobic additive (H1) to improve water resistance. The resulting product is referred to as TL1. By variation in the manufacturing process, a matrix type (REF2, TL2), distinguishable in composition and property profile but based on the same base material, is also investigated. Bioethanol (EtOH, purity 99.98 %) is used for solvent-based processing steps.

## 3 METHODS

Characterization of thermal and rheological properties of the matrix material is carried out using REF1 and TL1 as examples to determine the process parameters. Glass transition temperatures ( $T_{gs}$ ) were determined by differential scanning calorimetry (DSC) on a DSC 204 F1 Phoenix (Netzsch GmbH & Co. KG, Selb, Germany) according to DIN EN ISO 11357. Two heating cycles from 0 °C to 120 °C respectively 150 °C in the second heating cycle were carried out at 10 K/min each. The  $T_g$  was determined by the inflexion point method. The decomposition temperatures ( $T_{ds}$ ) are determined via the maximum in the differentiated mass loss-temperature curve from thermogravimetric analyses (TGA) according to DIN EN ISO 11358. The TGA/DSC 1 Star system (Mettler-Toledo, Columbus, Ohio, USA) was used. Heating was conducted from 20 °C to 1000 °C with a rate of 10 K/min. Measurements of the melt flow rate (MFR) by means of the capillary viscometer mi2 (Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany) were carried out according to ISO 1133 with 5 kg standard weight at 130 °C, 140 °C and 150 °C.

The matrix material is sourced from agricultural industry residues. Therefore, it offers potential for economical and sustainable biocomposites and avoids the problem of cultivation space requirements. Due to its structure, conventional processes such as resin transfer moulding are not suitable. To achieve high-quality, void-free composites, a new process is necessary. For this purpose, three different processes were realised to manufacture unidirectional-ply [0]<sub>8</sub> and cross-ply [0/90]<sub>2s</sub> composites in the size of 200 mm x 200 mm):

Process A: Using a vacuum-assisted film coating applicator (gap: 80 µm), matrix material films can be produced (Fig.1, top). By alternating stacking with flax fibre layers followed by consolidating using a heat press, composites can be produced (Fig. 1, A). This process has previously been used, for example, for hybrid metal / plastic composites [4].

Process B: A rolling mill (EXAKT Advanced Technologies GmbH, Norderstedt, Germany), otherwise used for the production of thermoset prepregs, is used to first impregnate the fibre scrims with the matrix material (Fig. 1, centred, gap: 0.4 mm, 50 rpm). Afterwards, several layers are compressed at an elevated temperature (Fig. 1, B).

Process C: As a novel manufacturing process, these two methods were combined by alternating stacking of impregnated flax fibre layers and films (Fig. 1, C).

For the solvent-based process steps of film production, fibre impregnation and additivation, the granulated material was dissolved in EtOH with a SpeedMixer DAC 150 (Hausschild GmbH & Co. KG, Hamm Germany,  $t = 10$  min, 3500 rpm). Undissolved particles were removed through a filter with a mesh size of 150 µm. The flax fibres were dried at 110 °C for 15 min before processing according to the data sheet specifications. The process parameters were determined under consideration of the material properties (Section 4.1). The heat press is heated to 130 °C at 5 K/min and left at 130 °C for 70 min with a press force of 40 kN (approx. 10 bar). For uniform pressure distribution and defined thickness of the resulting laminates, 4 mm thick frames were used in all processes. A peel-ply is added to the top and bottom layers. This ensures a uniform surface quality suitable for gluing GFRP tabs (1 mm) with epoxy-based adhesive (UHU Endfest 300, UHU GmbH & Co. KG, Bühl, Germany) for mechanical testing.

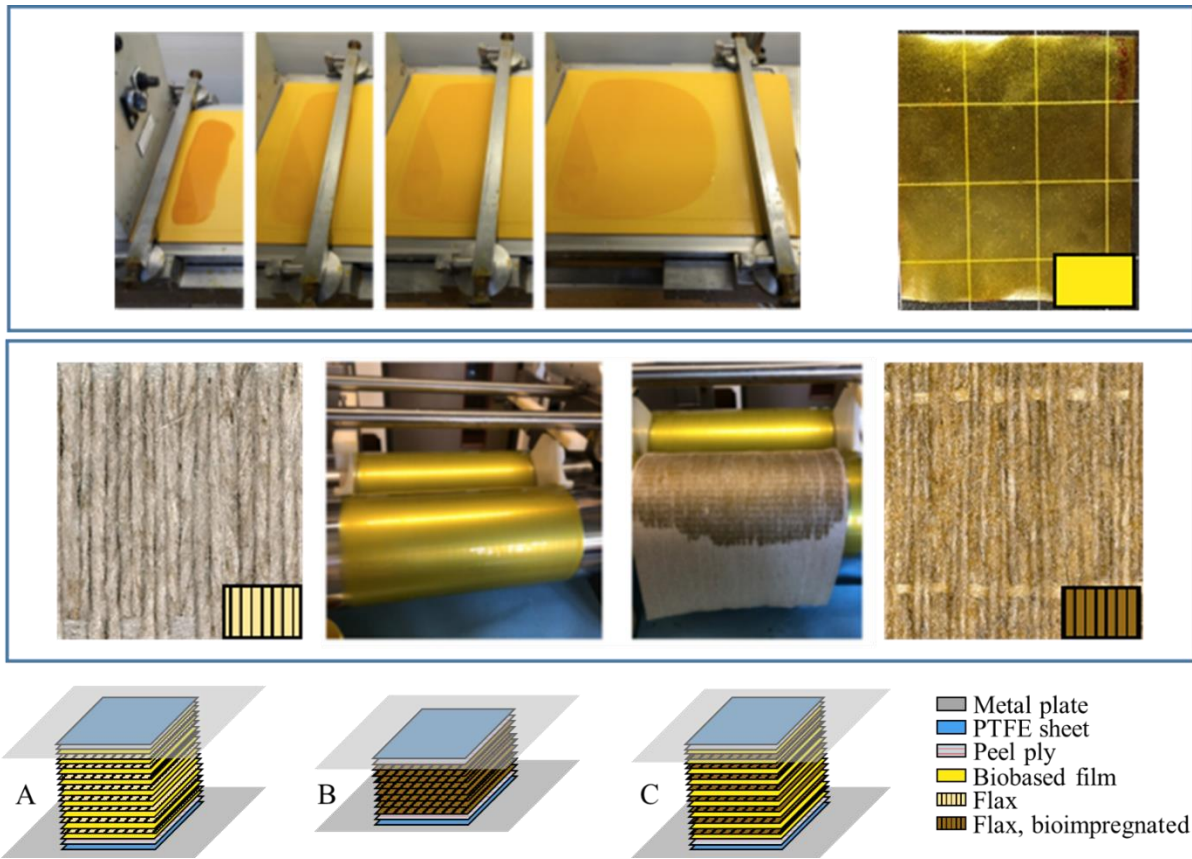


Figure 1: Top: Film production. Centred: Pre-impregnation of the flax fibres scrim. Bottom: Schematic overview of the processes.

All common methods for determining the fibre volume content experimentally are not applicable for flax fibre composites. Therefore, the volume contents of the fibres were determined gravimetrically from the masses of the fibres and films used, as well as from the mass of the matrix during impregnation. It should be noted that edge areas are included in the calculation.

Mechanical testing was performed according to DIN EN ISO 527. For testing matrix material properties, dogbone specimens were elaborated from films, conditioned for 24 h at 40°C under vacuum and tested using a paper frame for clamping on a Z2.5 universal testing machine from Zwick Roell GmbH und Co. KG (Ulm, Germany; testing speed: 50 mm/min). The strain measurement was performed with a video extensometer. The composites were tested on a Z100 universal testing machine (Zwick Roell GmbH & Co. KG) (clip-on extensometer, testing speed 3 mm/min). The corresponding test specimens were prepared with an F45 sliding table saw from Altendorf GmbH (Minden, Germany) and conditioned for 24 h at 40 °C under vacuum.

Biodegradability has been tested inspired by the standards DIN EN ISO 13432 and DIN EN ISO 16929 in the form of domestic composting within 12 weeks. Films of the matrix material (100 mm x 100 mm, one side on compost surface), flax fibres, impregnated flax fibres and samples of the composites (each 50 mm x 50 mm, in compost volume) were tested (Figure 2, left). The compost used complies with the DIN EN ISO 16929 standard. Expanded clay at the bottom of the container prevents waterlogging (Figure 2, centred). Before the weekly weighing, the samples were cleaned and dried for 24 h in a vacuum oven. Qualitatively, additional shredded composite samples without intermediate drying were left on the compost soil and visually examined (Figure 2, right).



Figure 2: Samples in compost (left); expanded clay (centred). Shredded samples (right).

## 4 RESULTS AND DISCUSSION

### 4.1 Thermal and rheological properties

The thermal properties of the matrix materials are summarised in Table 1. All selected additives themselves reduce the  $T_g$ . Due to their combination, the largest reduction is seen. Thus, the additives seem to affect each other with regard to the  $T_g$ . However, considering the measurements of the melt flow rate, they are necessary to ensure processability. P1 in particular increases the melt flow rate considerably. For later applications of the material, the  $T_g$  must be taken into account. Consequently, the application range is at a maximum of 60 °C and high-temperature applications are not suitable with this modified version.

	$T_g$ in °C	$T_d$ in °C	MFR (130 °C) in g/10 min
<i>REF1</i>	82.4	318.3	
<i>REF1</i> + 20 wt.-% P1	70.5	329.8	48.1
<i>REF1</i> + 20 wt.-% P2	67.5		
<i>REF1</i> + 20 wt.-% H1	79.0	297.0	
<i>REF1</i> + 5 wt.-% P1/P2/H1	77.5	325.9	
<i>TL1</i>	66.7	326.2	16.7

Table 1: Thermal and rheological properties

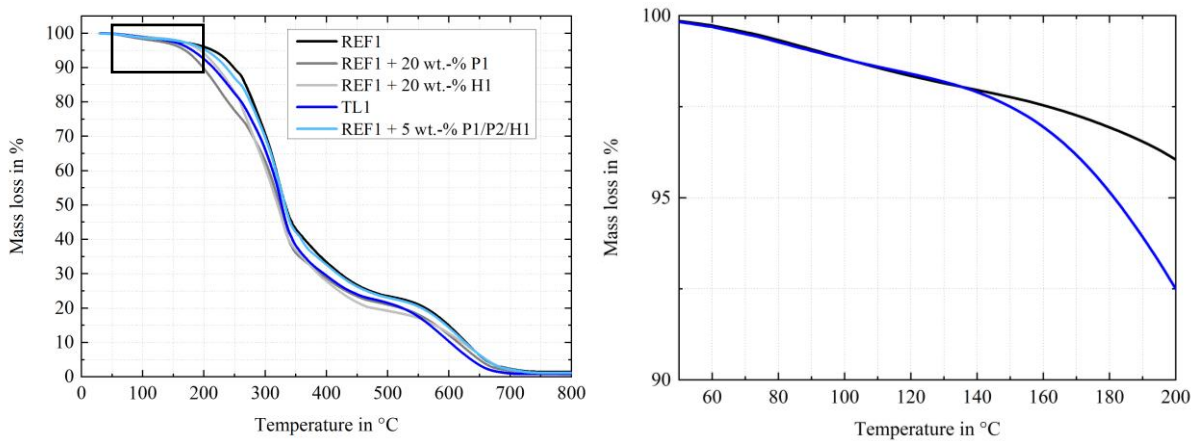


Figure 3: Mass loss over temperature from TGA. Total mass loss curve (left), detailed view on onset decomposition of TL1 (right).

The decomposition temperatures (Table 1) show good agreement with values in the literature [5, 6], which are also in the range of 320 °C. The TGA curves (Fig.3, left) show that the additives individually and in combination lead to an earlier onset of decomposition referred to REF1 5 wt.-%. Furthermore, it becomes clear that for the selected process temperature of 130 °C, no decomposition of the material has been initiated yet.

#### 4.2 Validation of the processes A-C

Fig. 4 (left) shows that flax fibres are natural products which are not completely homogeneous. In addition to growth anomalies, imperfections can also result from the processing of the plants into the present lay-ups through the process steps "breaking", "swinging" and "panting" [7]. As a result of the described process for pre-impregnation, after evaporation of the solvent, a non-sticky semi-finished product is formed from layers of fibres impregnated with the matrix material. The colouration and surface of the flax fibres change as a result of this process step (Fig. 4, right). By determining the masses before and after impregnation, it is possible to calculate a matrix absorption of  $0.38 \pm 0.05 \text{ g}_{\text{matrix}}/\text{g}_{\text{fibres}}$  normalised to the mass of the flax fibres which is equivalent to a fibre volume fraction of  $70.2 \pm 2.88 \%$ . Accordingly, the selected method leads to a reproducible pre-impregnation. Furthermore, films could be successfully produced with the method presented in Section 3, allowing processes A-C to be carried out and evaluated.

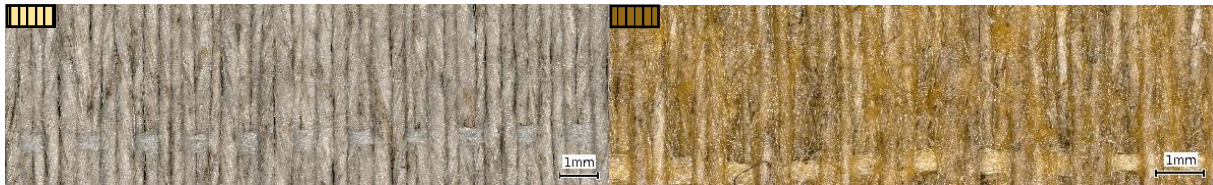


Figure 4: Flax fibres before (left) and after (right) impregnation.

A process challenge for flax fibre composites is to achieve sufficient fibre infiltration. With process A, the fibre infiltration is not successful (Fig. 5, top left). An adequate infiltration can be achieved by process B, but the bonding between the layers is poor (Fig. 5, centred left). The resulting composite achieves a fibre volume content of approx. 71 %. The matrix content cannot be further increased by impregnation in a three-roll mill by the solvent-based process alone. Process C improves this significantly (fibre volume content approx. 40 %), so that specimens for tensile tests can be prepared with appropriate quality (Fig. 5, bottom left). Therefore, the characteristic properties listed hereinafter refer exclusively to composites produced by process C (Fig. 5, right).



Figure 5: Tensile test specimens manufactured by processes A-C (left); composite plate made by process C (right).

### 4.3 Mechanical testing

Fig. 6 (left) shows the stress-strain diagrams obtained from the tensile tests of the matrix materials. It can be seen that TL1 with an elongation at break of approximately 180 % shows a viscoelastic material behaviour. In contrast, TL2 shows a brittle material behaviour with an elongation at break of approximately 2 %. The comparison of REF1 with TL1 shows that the addition leads to a reduction in tensile strength, but significantly increases the elongation at break.

As expected, this difference in material behaviour does not have a considerable effect on the quasi-static tensile properties of the composite. This can be seen in the comparison of the cross-ply samples in Fig. 6 (right). However, the influence of flax fibres, however, is decisive for the shape of the stress-strain curve. Bilinearity was observed for flax fibre composites independently of the matrix material. Various hypotheses explaining this characteristic have been postulated so far [8]. However, this behaviour is not untypical and must be taken into account for industrial applications due to the lower stiffness in the second linear section (for global strains  $\geq 0.25$  %).

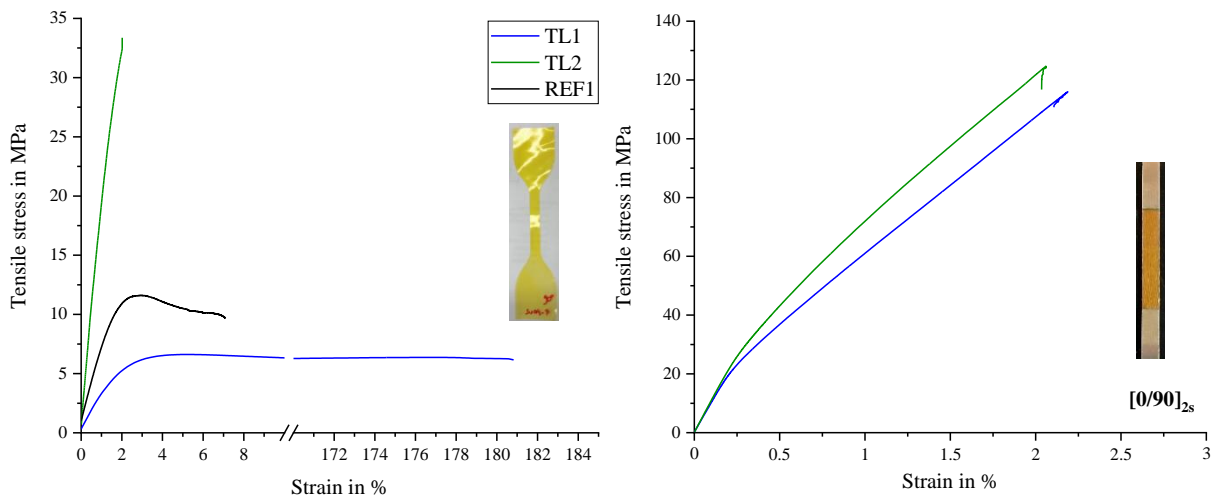


Figure 6: Representative tensile stress-strain-curves of matrix materials (left) and cross-ply composites (right).

Fig. 7 shows the maximum tensile strengths (left) and the Young's moduli (right) achieved for selected configurations. As shown in Fig. 7 (left), the tensile strength of TL2 is approximately 4.5 times higher than that of TL1 ( $30.72 \pm 2.63$  MPa vs.  $6.68 \pm 2.44$  MPa). The Young's modulus of TL2 is even six times higher ( $1.97 \pm 0.08$  GPa vs.  $0.32 \pm 0.06$  GPa). In the cross-ply composite, the delta between the tensile strengths of both materials (TL1:  $116.70 \pm 0.58$  MPa vs. TL2:  $126.19 \pm 3.05$  MPa) is less pronounced, which can be explained by the share of identical fibres in both systems using the principles of classical laminate theory. An analogous behaviour is seen for Young's moduli ( $9.91 \pm 0.31$  GPa vs.  $11.23 \pm 0.88$  GPa). Also shown are the transverse tensile results with material TL1, which are known to be mainly matrix dependent. As the transverse tensile strength of  $5.46 \pm 0.40$  MPa corresponds well to the strength of the neat matrix, this is an indication of good bonding between the matrix and the fibres. For comparison with other materials (Section 5), the strength and stiffness of the unidirectional composite in the longitudinal direction are also shown for the better-performing matrix material TL2. In this case, the mechanical properties are largely influenced by the fibres. A maximum tensile strength of  $239.51 \pm 7.46$  MPa and a Young's modulus of  $21.09 \pm 0.61$  GPa were achieved.

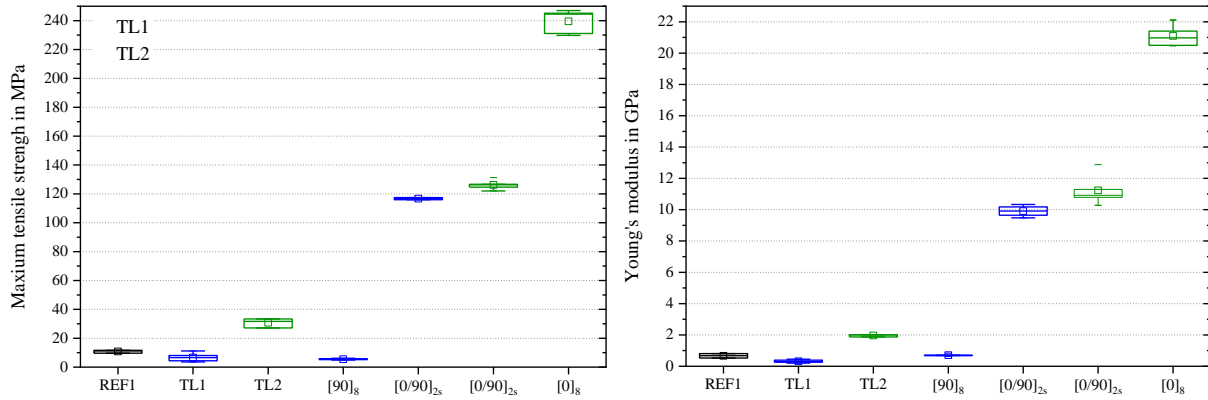


Figure 7: Maximum tensile strength (left) and Young's modulus (right) for matrix materials and selected composites.

Fig. 8 shows the fracture pattern of a representative cross-ply laminate. As expected, interfibre fractures occur first, which continue at approx. 45° up to the 90° layer and lead to delaminations at these interfaces. The damage growth regularly starts from gelled particles (white ellipses in Fig. 8). According to [5], these are formed by the aggregation of polymer chains, crystallisation or hydrogen bonding. If gelled particles smaller than the filter mesh are present in the protein-solvent suspension, they can act as nucleation particles. Further gel formation may occur through autocatalytic reactions. Gel formation depends on the water content, temperature and pH value [5]. It is possible to reduce gel formation by using a low water content in the process and lower temperatures. The pH value can only be adjusted by further additives and the process temperature of 130 °C is necessary for processability. Alternatively, consolidating under vacuum after drying the flax fibres is a promising possibility to optimise the production process and thus the mechanical properties.



Figure 8: Fracture pattern of a cross-ply specimen after tensile test. Ellipses indicate gelled particles.

#### 4.4 Biodegradability

As shown in Fig. 9, degradation due to biological activities can be observed for the raw materials (films and flax fibres) as well as for the impregnated flax fibres and for the composite. This is manifested by fading of the colour and changes in the constitution. Except for the composites, the samples could not be separated from the soil after seven weeks (flax fibres and films) or after eight weeks (impregnated flax fibres). For the composites, the degradation of the compressed layers is only superficial at first. After nine weeks, it is apparent that the degradation has also continued to the lower layers.

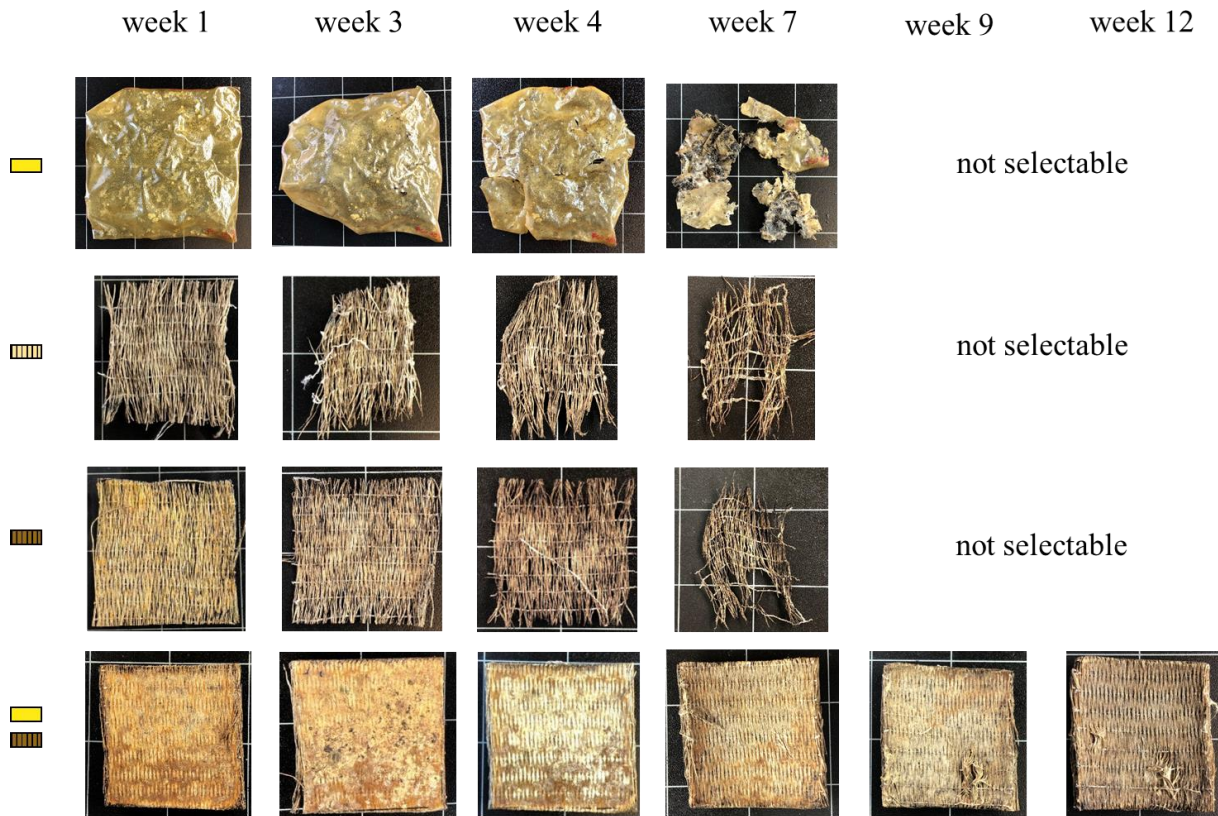


Figure 9: Specimens after ascending time in domestic composting.

This is also evident when looking at the relative mass loss over time (Fig.10, left). The degradation progresses continuously over time. After twelve weeks, a mass loss of 35 wt.-% is measurable for the composite. Due to non-removable soil residues on the samples, this value is to be regarded as the lower limit. In addition, the weekly drying of the sample interrupts biological activity. According to the literature [9], the optimum for enzymatic degradation is 40 °C, pH = 7 and 50 to 60 % moisture content in the soil. In wild disposal in nature, these conditions vary greatly depending on the season. In industrial composting, an increased loss of mass is to be expected due to accelerated biological degradation. Additionally, prior shredding of the composites increases the surface area, which accelerates biodegradation. After several weeks on the surface of the compost soil, the layers delaminate and the surface area increases further. As expected, the layers, which were initially on the outside, show more colour fading. This is shown qualitatively in Fig. 10 (right).

In comparison, the pre-impregnated flax fibre layer already shows a mass loss of 89 % after eight weeks. It should be noted, that fibres separated from the ply are not necessarily completely degraded. According to the standard, these fibres are < 2 mm in size and can therefore be neglected. In the case of composting in nature, the exposed fibres are also suitable as nesting material e.g., for birds. In general, a positive side effect is the incorporation of nutrients into the soil.



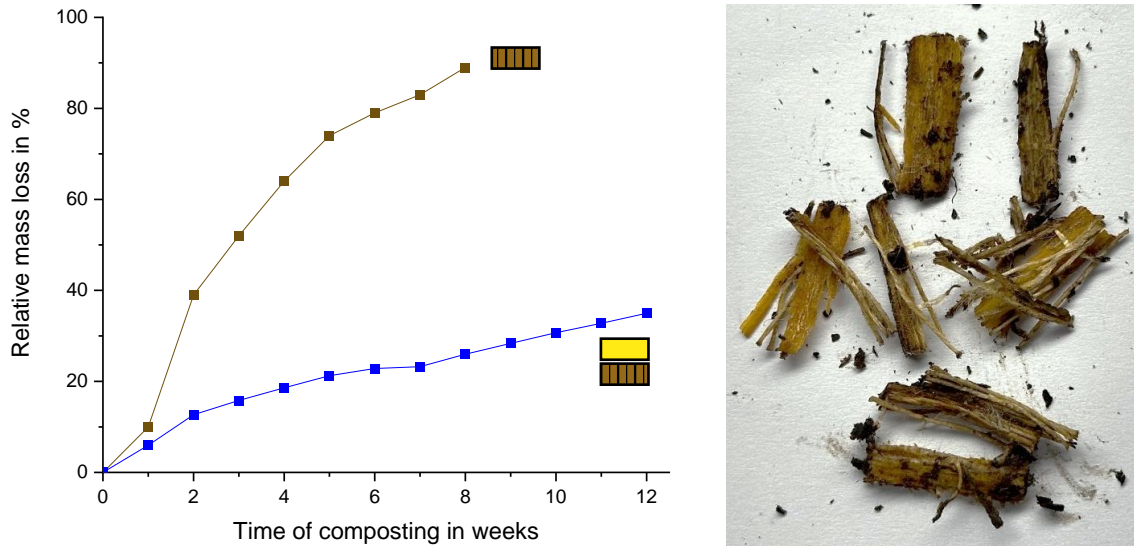


Figure 10: Relative mass loss of bioimpregnated flax fibres (brown) and biocomposites (blue) within the time of composting (left). Shredded composites after seven weeks of domestic composting (right).

## 5 COMPARATIVE CLASSIFICATION

To assess the mechanical performance of the manufactured natural fibre composites, a comparison with the literature has been carried out. In addition to other biodegradable composites [10], an epoxy-flax-composite [3], glass fibre reinforced epoxies (GFRPs) [11] and aluminium, as well as construction steel are also considered. To ensure the best possible comparability, all values, including density, for the composites shown (unidirectional composites in the longitudinal direction) are normalised to 50 % fibre volume fraction. In addition, for flax fibre composites only literature values for "noncrimp" flax fibres are listed in order to minimise the influence of fibre quality.

Fig. 11 (left) shows the specific tensile strength normalised to a density of 1 g/cm<sup>3</sup>. The manufactured composite is in the upper range of the biodegradable composites presented. The specific tensile strength of the manufactured composite reaches approximately 80 % of the epoxy-reinforced flax fibres. The flax fibres used in [3] are the same fibres used in this study, therefore, influences caused by different types can therefore be excluded. The GFRPs, with about twice the specific tensile strength, are clearly above the natural fibre composites. Steel and aluminium significantly underperform due to their high densities. On the other hand, these materials have isotropic properties compared to those of composites.

In contrast, the specific Young's moduli of the GFRPs (Fig. 11, right) are in the same range as the composites achieved with TL2. The EP/Flax composite has a slightly higher specific modulus. Compared to the other biocomposites considered, the achieved specific Young's modulus is in the lower range. However, the flax tape used in [10] consists of untwisted flax fibres [12]. The flax fibres used in the study have a twist angle of up to 10° [3], which may negatively affect the mechanical properties.

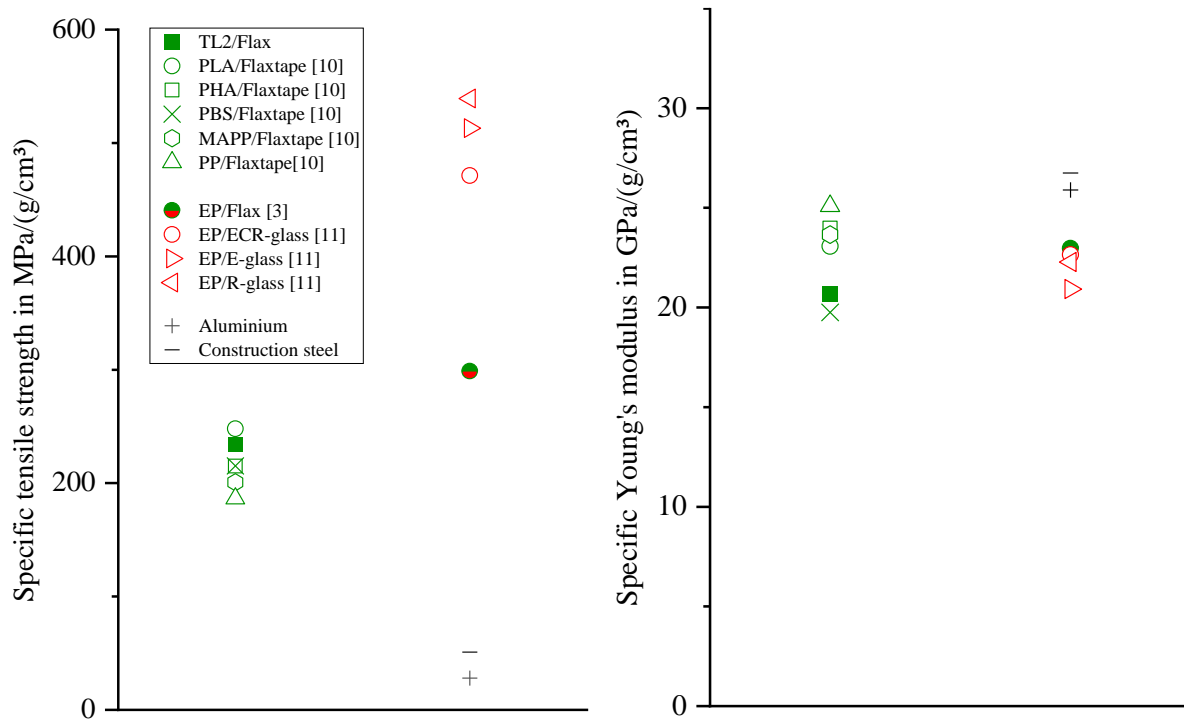


Figure 11: Comparison of specific strength (left) and stiffness (right) of the newly developed with comparative biocomposites and typical construction materials.

## 6 CONCLUSIONS AND OUTLOOK

The presented process of compressing impregnated fibre layers with stacked films has successfully allowed the production of void-free biobased composites. Mechanical tests show that the process leads to adequate fibre-matrix bonding. The mechanical properties achieved correspond to those of comparable systems. There is a variety of conceivable applications where traditional materials and composites can be replaced. In particular, the possibility of composting as a recycling strategy offers considerable advantages over conventional composites. Since the protein-based matrix material is obtained from agricultural waste, it is also a sustainable and cost-effective use of resources.

In detail, a simple process has been found that enables the manufacturing of biobased and especially biodegradable composites with competitive specific mechanical properties compared to petrochemical-based composites.

It has been demonstrated that a change in the manufacturing process of the matrix material leads to a significant change in the behaviour of the material. It can be assumed that an additional improvement is possible through further optimisation. Another possibility of further improving or adapting the properties of the matrix material is to vary the additives added and their compositions. A trade-off between processability and performance must be found. It is also conceivable to investigate the effect of parameter variations during process execution, for example, a reduction in cycle time. After all, the effects of environmental influences, such as UV irradiation or water absorption, must also be considered in order to test the limits of use.

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