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Abstract

Flax shives (FS) represent approximately 50% in weight of dry flax stems, making it the main by-product of the flax scutching industry. Being an available and low-added value lignocellulosic resource, flax shives are an interesting candidate for thermoplastic composite reinforcement. In this study, raw flax shives were fragmented by knife milling using two grids of 500 and 250 µm respectively, while a third batch, with a targeted particle size below 50 µm, was obtained by an attrition beads mill. The fragmentation methods used do not modify the biochemical composition of FS but do reduce their crystallinity due to both crystalline cellulose allomorph conversion and amorphization. The poly-(propylene) and 4%-wt maleic anhydride modified poly-(propylene) injection moulded composites produced with these reinforcing materials have a maximum tensile strength that evolves linearly with particle aspect ratio after processing. The tensile Young's modulus of the composites reinforced by coarser particles is 3268 ± 240 MPa, which is almost 90% that obtained for a reference 1 mm flax fibre reinforced composite. Furthermore, a basic micromechanical model was applied highlighting the reinforcing capacity of cell wall-like small tubular structures (e.g. flax shives). This study underlines the reinforcing potential of low-value by-product flax shives for value-added composite applications.

Keywords

Flax shives, injection moulding, morphology, mechanical properties, X-ray diffraction

1. Introduction

The development of the biocomposite industry in the past few decades due to ecological concerns has notably contributed to a growing interest in the plastic composite reinforcing potential of various agricultural by-products such as woody hemp core [1], sugarcane bagasse, sunflower and corn stalk [2], rice hull, corn cob and walnut shell flour [3]. Driven by eco-responsibility reasons such as the reduction of synthetic petrochemical consumption, the use of agricultural by-products represents a potential economically viable solution for local economy waste management, so long as transportation and transformation costs are limited. As flax cultivation areas are increasing (+8% in France from 2017 to 2018), so are the quantities of agricultural by-products from the flax scutching industry. Flax shives might then even be an alternative to the widely used wood flour in wood plastic composites (WPC), and their addition to wood flour could contribute to reducing the cost of such materials alongside recycling waste. Indeed, flax is an annual plant which temporarily stores carbon dioxide during growth [4, 5]. In the case of France, the flax cultivation areas are geographically concentrated along the English canal (from Normandie to the North), and this is a major advantage for material transportation from the production site to the end-use factory.

When cultivated for its fibre, flax stems are grown to be approximately one metre in height with a diameter of up to 3 mm [6]. When mature, stems are harvested, undergo a retting step followed by a scutching process in order to extract the high added-value bast fibres. The retted stems are crushed by successive fluted rollers, and then beaten from bottom up in order to separate the fibres from the rest of the stem constituents, mainly from flax shives (FS) which are a cause of quality defects in the fibre transformation processes. FS represent around 50% in weight of retted flax stems [7], which makes them the main by-product of the flax fibre production process. Traditionally used for soil amendment, animal bedding or particle boards for building insulation [8], FS have also been studied as a resource for various innovative applications including activated carbon [9], 3D printed lightweight concrete [10], and bio-fuel production [11]. FS have a low added value, a low density and, above all, are a widely available resource which flax scutching companies wish to broaden the areas of application of, and this makes them a genuine potential reinforcing material in bio-composites.

Flax shives, also referred to as woody core, have a highly lignified structure made of the inner tissues of the stem, namely the pith, the xylem and the phloem, the last two having a role in the conduction of raw and elaborated sap, respectively. Studying the transverse section of flax stems, Goudenhooft et al. measured the tissue content to be between 70 and 85% depending on the flax variety, and the xylem represents about 75% of the total tissue content [6, 12]. They also found, by stem flexural bending tests, that the woody core has a structural role and accounts for up to 30% of dry flax stem bending stiffness due to architectural differences and lower density.

The composition of flax shives is approximately 25% lignin, 50% cellulose, and 20% hemicellulose [3, 13], but this varies depending on the analytical method, plant maturity and even location of FS in the stem. Day et al. [14] found that lignin content ranges from 24% to 32% in the inner tissues depending on maturity and location in the stem, against only 1.5% to 4.2% in the dry cell wall resides in the outer tissues (specifically fibre bundles imbedded in the parenchyma, the cortical parenchyma, and the phloem).

Raw bulk flax shives demonstrate a considerable particle size distribution, with particles as long as 40 mm [10] and thus can be difficult to use as such for efficient polymer reinforcements. Consequently, a mechanical size reduction step such as comminution by grinding is useful in controlling particle granulometry, size distribution and aspect ratio (ratio of length over particle width or fibre diameter).

Knife milling can be used as a first reduction step (from the meter scale to that of the centimetre) of forages or stems [15]. In this grinder, particles are fed continuously and the comminution is mainly achieved by shear mechanisms. The size of the ground particles is determined by the size of the hole of the sieving grid (from a few millimetres to hundreds of micrometres) at the output of the milling chamber. On the other hand, small particles (10-500 µm) can be obtained by media milling, which consists of breaking down batches of particles by compression and attrition mechanisms thanks to a milling media (ball or beads) put in motion by a rotor, a vibrating or rotary tank. This technique allows to reach very fine particles but the total energy consumption is higher due to long residence time required to obtain such fine granulometries [16]. In addition it has also been proven that such technologies reduce the crystallinity of plant cell wall cellulose [17, 18].

In composites, the bonding efficiency will determine the quality of stress transfer between reinforcement and matrix. When plant fibres are embedded in a polymer matrix, they generally increase its stiffness and reduce tensile deformation. An optimal fibre volume fraction has been observed in injection moulded PP composites after which tensile strength decreases; this is around 33%-vol specifically in the case of flax-PP composites [19, 20, 21]. The impact of reinforcing fibres on composite mechanical properties depends in particular on fibre orientation which in the case of short fibre reinforced injection moulded composites depends on the severity of the skin-core effect. Morphology and structure of plant reinforcement also plays a major role in fibre orientation [22]. Fibre length, tendency of packing, viscosity, process parameters, all influence the thickness of the skin layer which contains the most fibres parallel to the melt flow direction and accounts for higher mechanical properties [22, 23, 24]. The higher the fibre aspect ratio, the higher the mechanical properties. Stark et al. [25] compared the role of wood flour and wood fibre having approximate aspect ratios of 4 and 16 respectively. When incorporated with MAPP in injection moulded composites, they found that tensile strength of the latter increased between 30 and 60% depending on the amount of wood fibre compared to wood flour composites. While the aspect ratio of flax fibres will depend on fibre fineness and processing [26, 27], that of flax shives will depend highly on the mode of comminution.

The aim of this study is to evaluate the reinforcing potential of flax shives, a by-product of flax fibre crop. In order to situate the mechanical properties of FS injection moulded PP composites, a panel of different plant cell walls were tested for comparative purposes. This analytical investigation is based on a two-level strategy. First, the FS structure was examined by particle size analysis following two methods of comminution (knife or attrition beads milling). An ultrastructural study of these fragmented FS was carried out by X-ray diffraction analysis. Additionally, the constitutive polymers of FS were characterised by biochemical analysis. Second, at the scale of the composites, mechanical properties of injection moulded composites were measured, specifically interrogating the impact of FS particle size and filler volume fraction (from 0% to 31%). Finally, a theoretical approach to determine FS critical length was discussed with the help of a simplified mechanical model, to understand the reinforcing potential of small and hollow cell wall structures such as shives.

2. Experimental

2.1. Matrix polymer

The matrix used in this study is polypropylene, chosen because it is a commodity polymer widely used in the automotive industry. PPC 10642 was supplied by Total Petrochemicals (France) with a MFI of 44 g/ 10 min at 230°C and 2.16 kg, and a polymer density of 0.94. Because plant cell walls have an important polysaccharide content giving them a hydrophilic nature, maleic anhydride modified polypropylene (MAPP) was added to the formulation as compatibilizer for its amphiphilic nature enabling bonding with both the hydroxyl groups of the filler and the hydrophobic polymer matrix [28]. MAPP (Orevac CA 100) was supplied by Arkema (France) and has an MFI of 10 g/10 min (at 190 °C and 0.325 kg), 4% of MAPP were added to the formulation during the compounding process as it represents a good compromise between bonding improvement and cost of polymer [29].

2.2. Reinforcing materials

The flax shives used in this study were provided in bulk by the flax scutching company Van Robaeys Frères (France) following the scutching of the 2018 flax harvest year, before being milled with a laboratory scale rotating cutting mill (Retsch Mühle, Germany). The mesh size of the grids used were either 500 µm or 250 µm. To obtained finer powder, the powder ground with the knife mill (250 µm-grids) have been submitted to an additional milling step in an attrition beads mill, as the previous technique is not adapted to obtain such fine granulometries [30]. The equipment employed is a laboratory prototype, composed of a milling chamber of 3 L in which 175 g of the powder to grind and 7.5 kg of small steel beads (6 mm) are put in motion by a rotor at 300 rpm. The milling time (100 min) was determined so that at least 90% of micronized particles have a diameter below 50 µm.

The flax fibre (*Linum usitatissimum L.*) used is from the Alizée variety, which was harvested in 2017 in Normandy (France), and was scutched and hackled before being cut to 1 mm in length and supplied as such by Depestele (France). In the rest of this study, the term “fibre” will designate both elementary fibres and flax fibre bundles as both are present in the studied batch; otherwise differentiation will be made by specifying “elementary fibres” or “bundles”.

An additional sample of wood flour was studied for comparative purposes as it is commonly used in the wood plastic composites industry. This sample is composed of a mixture of untreated *pinus pinaster* and *picea sitchensis* wood chips originating from sawmill residues, therefore precise history and composition is unknown. They have further been dried, fragmented by hammer milling with a 1 mm grid and sieved. The fraction under the 800 µm sieving mesh size was studied here. All reinforcing materials and their corresponding abbreviations as they will be used throughout the article are given Table 1.

2.3. Particle size analysis

Particle morphology was studied by a dynamic image analysis device, QICPIC (SympaTec GmbH, Germany). Two shape factors were determined (i) the particle length, defined as the shortest path between the most distant end points of the particles after skeletonization, (ii) an aspect ratio (length over diameter). The aim was to understand the effects of comminution on the granulometry of FS. Both the materials samples before and after extrusion and injection moulding (see section 2.6) were investigated. For the latter, samples were obtained from composites after dissolving the PP matrix with o-xylene at 150°C during 3 days by reflux. The extracted particles were then thoroughly washed with boiling xylene followed by acetone and left to dry overnight in a 60°C oven. All samples were oven dried at 60°C overnight before measurement in order to limit analysis bias caused by initial water content. Two protocols have been adapted for the particle morphometric description by the QICPIC. For the raw particles (flax shives and flax fibres), the most appropriate way was to disperse those samples with a vibrating chute VIBRI unit combined with a dry dispersion unit GRADIS, because of their important particle size and easy scattering. All the others samples micronized or extracted from composites were more appropriately analysed with a liquid dispersion unit, MIXCEL. Indeed, these batches displayed a tendency to particle aggregation so they were first dispersed in ethanol. To obtain accurate data in the morphological measurements, the QICPIC lenses (from M9 to M5) have been adapted to the size of each sample. The selection of the appropriate lens is based on initial visual coarseness of sample and supplier specifications. As we assume that the particle size variation remains weak before and after processing, the same lens was used in this case in order to obtain data in the same range. The number of analysed particles varied between 20,000 and 10 million depending on samples, measurements were made in triplicates to ensure reproducibility of the results. PAQXOS software (SympaTec GmbH, Germany) was used to calculate particle length and aspect ratio in real time.

2.4. Biochemical composition

The monosaccharide content of the sample lots (Table1) were assessed by wet chemical analysis, aside from the extracted ones after extrusion-injection because of arguable extraction bias due to the o-xylem solvent used. Before hydrolysis, the large size of the R-FS, FF and WF particles requires a first step of homogenization done by cryogrinding (SPEX 6700 freezer Mill) of approximately 1g of materials. The whole panel of powdered samples (approx. 5 mg per assay) were then hydrolysed in 12 M H2SO4 (Sigma Aldrich) for 2 h at 25°C (heat plate) followed by additional hydrolysis of 2 h at 100°C with 1.5 M H2SO4 in presence of inositol as internal standard. Galacturonic Acid (GalA) and Glucuronic Acid (GlcA) was determined by an automated m-hydroxybiphenyl method [31] and merged as Uronic acid (UrAc), whereas individual neutral monosaccharides (arabinose, rhamnose, fucose, glucose, xylose, galactose and mannose) were analysed as their alditol acetate derivatives [32] by gas-liquid chromatography (Perkin Elmer, Clarus 580, Shelton, CT, USA) equipped with an DB 225 capillary column (J&W Scientific, Folsorn, CA, USA) at 205°C, with H2 as the carrier gas. Standards of carbohydrate solutions with three known concentrations were used for calibration. Analyses were performed in three independent assays. The total monosaccharide content is the sum of each monosaccharide amount, and is expressed as the percentage of the dry matter mass.

The lignin content was quantified in the panel of samples (Table 1) from the homogenised micronized particles. Lignin was quantified by colorimetrical analysis following the acetyl bromide method [33] on mass weight samples of approx. 20 mg per essay. The chemicals were laboratory grade from Sigma Aldrich and the analyses were performed in at least three independent assays, with lignin expressed as the percentage of the dry matter mass.

2.5. X-Ray Diffraction

Wide-angle X-ray diffraction (XRD) measurements were performed in triplicates under ambient conditions on a Siemens D500 diffractometer CuKα radiation. Samples were loaded on a silicon wafer and scans were collected from 2θ = 10 to 30° with step size of 0.03° at 2 s/step, at 30 kV and 20 mA. Crystallinity was calculated based on the method developed by Segal et. al using Eq. 1, where I_{tot} is the intensity at the primary peak for cellulose I (at 2θ ≈ 22.5°) and I_{am} is the intensity from the amorphous portion evaluated as the minimum intensity (at 2θ ≈ 18.5) [34][35].

$$C = \frac{I_{tot} - I_{am}}{I_{tot}} \times 100 \quad \text{(Eq. 1)}$$

2.6. Preparation of composites

Before processing, the reinforcing materials and PP-MAPP matrix were oven dried at 60 °C for at least 12 hours. They were then compounded with a single-screw extruder (Fairex, England) at 190 °C and an extrusion speed of 25 rpm. The length and diameter of the screw were 600 and 20 mm respectively, inducing an aspect ratio L/D of 30. After granulation and oven-drying in the same conditions, the material under-went a second extrusion step using a TSA (Italy) co-rotating twin-screw extruder with a screw diameter of 20 mm and L/D ratio of 40. A temperature profile going from 180°C to 190°C and a die temperature of 180° C were imposed with a screw rotation speed of 300 rpm. The material was once more granulated, oven-dried, and ISO 527-2 type 1B normalised specimens were obtained using an 80 Tons Battenfeld (Austria) injection moulding machine with a constant barrel and mould temperature set at 190°C and 30 °C, respectively.

2.7. Mechanical Characterization

The injection moulded T-bone specimens were submitted to tensile testing following the ISO 527 standard on an MTS Synergie 1000RT machine with a controlled environment (temperature of 23°C and relative humidity of 48%). Tensile speed was of 1 mm/min and nominal gauge length was 25 mm. A 10 kN sensor was used to measure the applied force on the specimen, and an extensometer was used to measure deformation during the tests.

2.8. Density measurements

The density of raw FS-500 was measured by helium pycnometer measurements based on the method described by Le Gall et al. [36]. Measurements were made in 10 replicates and the average value of 1.43 g/cm^3 was obtained. The rule-of-mixtures was then applied to calculate the volume fraction in the composites knowing the density of the PP-MAPP matrix as follows (Eq. 2):

$$\rho_c = \rho_{fs} V_{fs} + \rho_m (1 - V_{fs}) \quad \text{Eq. 2}$$

With ρ_c, ρ_{fs}, and ρ_m the density in g/cm^3 of the composite, the flax shives and the matrix respectively, and V_{fs} the volume fraction of the reinforcing flax shives, calculated knowing the mass fraction and density of the components.

2.9. SEM Observations

The raw reinforcing materials were observed using a Joel JSM 6460LV (France) scanning electron microscope (SEM) after comminution and prior to composite processing after being sputter coated with a thin layer of gold in an Edwards Sputter Coater. The fracture surface of specimen following tensile testing were also observed by SEM.

3. Results and discussions

3.1 Characterization of the reinforcing materials

3.1.1 Validation of the experimental procedure

First, a comparison between the number and volume length distributions is proposed in order to determine a valuable method of particle size analysis using the dynamic analyser used (QICPIC). Particle morphology analysis provides significantly different information depending on measurement parameters such as equipment used, image resolution, automatic or "by-hand" measurements, causing specific particle size populations to be potentially left out [36, 37, 38].

The length distributions given in number and volume are schematically displayed by box-plot diagrams in Figure 1. Because a unique average value does not give any information on distribution span, symmetry, skewness or extreme values, box plots are preferred. It is a simple visual tool adequate to use in statistical analysis to evaluate data (median, span…) without making any suppositions on its distribution, especially when it does not follow a normal or log-normal law. The 10th (first decile), 16th, 50th (median), 84th, and 90th (last decile) percentiles of the cumulative distribution in length are shown respectively from bottom up.

The number distributions (Fig. 1a) emphasise the quantity of small particles present in each batch, as each particle is given the same "weight" regardless of size. On the contrary, in the volume distribution (Fig. 1b), a "weight" is attributed to each particle corresponding to the volume of the particle divided by the total volume of particles analysed. In this study, the particle volume is assimilated to a cylinder of which the length and diameter are those measured for each particle. Therefore, in this distribution small particles are somewhat obscured as their weight is much lower than that of larger particles. Both the distribution in number and in volume are complementary for readers to have a cognitive understanding of a population of particles, however in the aim of materials reinforcement when dealing with natural fibre, the distribution in volume is most desirable compared to the distribution in number [40] as this parameter is most representative of the volume fraction of reinforcing material and its role in the mechanical support of the composite.

Note also that small particles are composed of only few pixels and the precision in the determination of the shape factors are lower than for larger particles like fibres composed of hundreds of pixels. By choosing an adequate lens for the device, it is possible to increase the number of pixels of an element thanks to a shorter length scale of the pixel size, but in this case, it becomes difficult to focus on larger particles. Thus, for powders exhibiting broadly scattered particle sizes, the limitations of the device do not allow to have a high resolution for both small and large particles at the same time. This point should be kept in mind when comparing the different particle size distributions.

Figure 1a reveals that 84% of raw flax shives (R-FS) are made up of particles less than 90 µm long, whereas the volume distribution shows that 16% of particles are less than 3052 µm long. Except for FS-50, all initial reinforcing materials have at least 80% of their number distribution which lays completely out of their volume distribution. Shives are obtained during the scutching of flax, which also produces up to 10%-wt of dust from the retted straws originating mainly from cultivation step in the fields. An unknown part is left in the shives and is found in the initial R-FS and will be present in all batches as it won't be affected by comminution. This proportion of particles smaller than 200 µm (which represents the particle length limit commonly admitted as defining fines [41]) is present in all studied reinforcing materials as the FS-500, FS-250 and FF median lengths in number are of 8 or 9 µm against 484 µm, 455 µm, and 976 µm in volume respectively.

The sample length distributions in volume (Fig. 1b) shows the initial R-FS median length is reduced by 10 when using the knife-milling step in the case of FS-500. The latter's median length is then comparable to that of the FS-250 sample at 455 µm. The 84th percentiles of FS-500 and FS-250 are at 1518 µm and 1134 µm respectively, which is respectively 3 and 4.5 times more important than the initial milling grid mesh size. This can be explained by the grids' pattern which has a grating effect on

R-FS. Furthermore, the 84th percentile of FS-50 is of 30 µm, making the length of this sample complementary to that of the last two samples for this study.

The morphological study of particles can be carried out by image analysis after observation under optical microscope of a sufficiently significant population of particles. Automated laser measurements have the advantage to be less operator dependant. Le Moigne et al. [37] found that 'by hand' measurements induced a discrepancy and had a tendency to magnify fibre dimensions due to operator dependence compared to using a specific software for fibre detection (50% of the number weighted length of flax fibres measured by hand were more than twice the length of the same particles detected by the software). Dynamic image analysis is a time-efficient method to obtain a wide amount of particle morphology information such as shape descriptors and distributions in number, length, surface or volume [38]. In the rest of this study, analysis is carried out on the basis of volume distributions.

3.1.2 Morphological analysis of raw reinforcing materials

Figure 2 shows the particle length distribution in volume as well as the overall aspect of the reinforcing materials as observed with SEM images. Prior to comminution, R-FS presents a very wide fibre length distribution with a median of about 4850 µm and a main mode at 6300 µm, which is similar to the "by-hand" optical measurements by Evon et al. [42] of 5800 ± 4013 µm of average length. The reference flax fibres present a homogeneous fibre length with a unimodal distribution having a median of 976 µm coherent with the targeted fibre length of 1 mm. Wood flour exhibits a heterogeneous length distribution, with a visually important aspect ratio, and a median length of 440 µm. Wood flour used in this study originates from saw milling waste and was used as-received without any further sieving. FS-500 and FS-250, both fragmented using a knife milling device and milling grids of 500 µm and 250 µm respectively, show several distinct particle populations: fine particles having a mode at approximately 70 µm for both samples, and coarser particles with a mode of 1450 µm and 1000 µm, respectively. This similar behaviour can be explained by the comminution process for which raw FS are continually fed to the machine inducing an unknown residence time, causing certain particles to be more fragmented than others. In addition to this, we can assume that depending on the origin of FS (e.g. type of cell, position in the plant, plant maturity), the differences in cell wall rigidity (varying amount of lignification depending on the role of the cells in the plant) and specific mechanical strength of initial R-FS will have an effect on the kinetics of fragmentation and disaggregation. Flax xylem compressive strength at break measured from 3-point bending tests carried out on peeled flax stems is approximately 60 MPa, which is a third of the strength of the whole stem [43]. The mostly xylem origin of FS also explains why the fine particle population visible on the SEM images of both FS-500 and FS-250 is absent in that of FF. Furthermore, contrasting initial processing steps may bring further insight on this phenomenon as flax fibres were hackled before being cut, which further removes residual cortical tissues from fibre bundles and therefore reduce the amount of fines in the sample. Figure 3 shows that the alveolar structure of FS from the plant's xylem is preserved after knife-milling providing a reinforcing material with hollow tubular sections corresponding to dry conduction vessels or supporting xylem cells. Indeed, in a knife mill, the compression mechanism remains weaker in comparison to shear mechanism and the type of mill is known to preserve the structure of the plant materials [44].

Furthermore, Figure 2 shows that particle length distribution of FS-50 is very narrow, with a first decile, a median, and a last decile of 9 µm, 17 µm, and 33 µm respectively, accounting for a homogeneous particle fragmentation justified by the intensity of the 23-hour ball milling process. This panel of results exhibits the strong impact of the material preparation (cutting, knife milling, or ball milling) on particle morphology and structure.

3.1.3 Biochemical analysis

The monosaccharide and lignin content of the different samples are given Figure 4. Considering that glucose accounts for sample's content in cellulose, then flax fibres FF are made of 70% of cellulose on average (out of total dry matter content) compared to only 30% for flax shives FS and 42% for wood flour WF; and approximately 3% of lignin for FF, against 30% for WF and R-FS. The latter also contain about 16 times more xylan than FF which is in agreement with measurements carried out by Buranov et al. [30, 44]. The differences in biochemical composition can be explained by the contrasting origins and functions of cells in the flax stem. Due to their high mechanical role, flax fibres possess well developed secondary cell walls made up of cellulose microfibrils and can be considered as gelatinous fibres [46] with low lignification. In contrast, xylem cells have a role in the mechanical support of the plant and so have a secondary cell wall, but are responsible for raw sap conduction and therefore are highly lignified from the base to the top of the plant [47], also highlighted by the progressive lignification of the xylem throughout plant growth [14].

Since the wood flour comes from fluctuant sawmill wastes, it is a blend of both soft and hardwood but the precise species origin is unknown, as well as its ratio. Therefore its biochemical composition was determined for information purposes and is in agreement with ranges found in the general literature [48].

Furthermore, the amount of cellulose, lignin and non-glucosidic monosaccharides does not significantly evolve in the FS samples following fragmentation, even in the case of intense milling in the attrition beds mill (FS-50). It is interesting to notice that contrary to ball milling known to cause a drop in cellulose content in wood or flax fibres, the intense milling employed here seems to preserve the total chemical composition of the powder. This is probably due to the shorter milling time (100 min compared to several hours in ball milling).

3.1.4 XRD

The diffraction pattern of cellulose I (Fig. 1a) includes five major reflections for the crystalline phases at 2θ ≈ 15° (1$\bar{1}$0 diffraction plane following the recommendations of French [49]), 17° (110), 21° (102), 22.5° (200) and 34.5° (004), with the amorphous phase observed at 2θ ≈ 18.5° [35]. These reference peaks were used to analyse the XRD spectra of the various flax fibre samples (Fig. 5a).

All samples exhibit a primary peak at 2θ ≈ 22.5° corresponding to the crystalline 200 plane of cellulose I, however the peak is sharp and distinct for raw flax fibres, slightly broader for raw flax shives until 2θ ≈ 12° (belonging to cellulose II or III), supposing the presence of both cellulose I and cellulose II or III in raw flax shives. This peak gets broader (left-ward) with the severity of attrition beads milling (Fig. 5a). In addition, raw flax fibres, and to an extent raw flax shives, exhibit the 1$\bar{1}$0 and 110 secondary peaks, while these peaks are less distinct for ball milled flax shives, and not discernible for FS-50. The noted qualitative observations and subsequent measurements (Fig. 5b) suggest a reduction in crystallinity (increase in level of disorder) of the shives with severity of ball milling, as was observed with after two hours of ball milling on crystalline cellulose [50]. Specifically, while raw flax fibres and shives have a crystallinity of 77.2% and 60.0%, respectively, the cellulose crystallinity reduces to 41.7%, 38.8% and 28.9% for FS-500, FS-250 and FS-50, respectively. The latter is comparable to the crystallinity of wood flour (31.3%).

With increasing severity of ball milling, while no distinct shifts in diffraction peaks are observed, there is left-ward broadening of the $2\theta \approx 22.5°$ (belonging to 200 plane of crystalline cellulose I), and the presence of an additional and increasingly important peak at around $2\theta \approx 12°$ (which belongs to cellulose II or III) [51]. Notably, wood flour exhibits this prominent peak as well (Fig 5a). These indicate that cellulose II or III is becoming prominent with ball milling; typically, cellulose I irreversibly converts to cellulose II upon mercerisation or urea treatment [50, 51], and cellulose I can reversibly convert to cellulose III upon liquid ammonia treatment [52, 51]. Notably, there are a number of studies which have reported the conversion of cellulose I into cellulose II,III or IV after ball milling under specific conditions [17, 53, 51]. In particular wet ball-milling using water [17, 54, 55, 56] (or NaOH/urea) [53], even at ambient temperatures (25 °C), can partially transform cellulose I to cellulose II relatively quickly (e.g. 30 minutes of ball milling). Higher temperatures (e.g. 80 °C and above) can further assist the transformation, particularly into cellulose IV [17]. The temperature of the powder measured at the end of the milling step in attrition beads mill was of 70 °C and could explained the change observed in the crystallinity of the cellulose. In our studies, we haven't measured how temperature evolves during knife milling.

Comminution, by amorphization of particles, results in a decrease in degree of polymerization and therefore of sample crystallinity. But the comminution process parameters (temperature, humidity, milling media) also impact cellulose type conversion that are revealed here. These crystallinity modifications have an effect not only on material sensitivity to moisture absorption but also on sample thermal stability and adhesion with the polymer matrix and thus composite mechanical properties.

3.2 Properties of composites

3.2.1 Reinforcement material morphology analysis after processing

Before evaluating the mechanical properties of the PP-MAPP injection moulded composites processed with 30%-wt reinforcing materials, the morphology of the reinforcing particles after processing are given in Figure 6a and b. Figure 6a shows that FF, the 50/50 mix of FF and FS-500 and FS-500 have important length spans with a median length of 289 µm, 317 µm and 297 µm respectively. The 90^{th} percentile of these samples increases in the same order, indicating an important number of long particles present in the FS-500 sample which explains that FS-500 + FF has a higher median than FF itself.

The length of FF presents a drastic drop of 70% after processing from their initial length given in figure 1b. The twin-screw extrusion is assumed to be the cause of this as it generates high shear stresses [20]. Some authors have studied this effect and reported a length reduction between 50% and 70% of average flax fibre initial length after mono-screw extrusion processing [22, 40]. As shown in Figure 7, the twin-screws used in this study are designed with several kneading areas, one of them being even reversed, leading to improved mixing and additional shear stresses. Furthermore, defects in flax fibres, known as “kink-bands”, have been shown to influence the rupture of fibres during compounding as localized stress concentrations cause fibre rupture after processing to coincide with the mean distance between two consecutive kink-bands [57, 58].

Surprisingly, FS-500 only underwent a 39% median length reduction due to processing, and an important quantity of longer particles is present after processing when compared to FF. Shives consist of fragmented assemblies of xylem cells, which are highly lignified in contrast to fibres. Even so, FS-250 and WF underwent a 75% and 70% decrease in length respectively, therefore the fragmentation mechanisms of the FS-500 sample are complicated to judge without further analysis. Moreover, the proportion of smaller particles is less affected by shear stresses: this is clearly visible in the case of FS-50 as their length distribution stays practically unchanged with a median length of 20 µm before and after processing. This suggests that the process may reduce particle length up to a critical length independent of initial fibre length number of processing cycles.

Figure 6b shows the evolution of the distribution of particle aspect ratio before and after processing. It is possible to see a 36%, 40 % and 77% decrease between Raw-FS and FS-500, FS-250 and FS-50 respectively depending on comminution mode. The median aspect ratio of WF is of 5.5, which is comparable to that of FS-250, but to the limit that WF shows a higher amount of high aspect ratio particles, as the WF last decile is of 15.4 against 11.9 for FS-250. After processing of the 30%-wt reinforced PP-MAPP composites, reinforcement material aspect ratio globally decreases. Indeed, the L/D of FF and WF decreases by 8% and 11% when compared to before processing, and this is even more accentuated for FS-500 and FS-250, which show a 21% and 38% drop respectively. Interestingly, L/D distribution tends to tighten for FS towards smaller values due to the reduction of particle length because during processing, as discussed earlier.

The median aspect ratio of FF is the highest at 11.5 due to the combined action of the delamination of bundles into individual fibres [37]. For the other reinforcing materials, the median aspect ratios are of 4.8, 3.5 and 2.3 for FS-500, FS-250 and FS-50 respectively, while that of WF is equivalent to FS-500 at 4.9, although a higher proportion of elongated particle is present as the 84^{th} percentile is of 8.4 for WF against 7.3 for FS-500. Flax fibres therefore have a load transfer potential more than twice as great as wood flour but other parameter must be taken into account such as fibre-matrix adhesion and the proportion of fines possibly accountable for fracture initiation. The relevance of the 50/50 mixture of FF and FS-500 is to increase by 30% the median aspect ratio of FS-500 and by up to 110% the last decile, meaning the potential load transfer of the material is highly improved all the while the price of the raw material is considerably diminished compared to the initial cut fibres. Indeed, the market value of raw flax shives can be as low as one thirtieth that of scutched flax fibres. Furthermore, varying proportions of FS and FF would allow for specific composite mechanical properties all the while controlling the reinforcing material's cost.

3.2.2 Tensile properties

Table 2 shows the tensile mechanical properties of the injected composites of PP-MAPP matrix reinforced with 30%-wt of the different reinforcing samples. As expected, the incorporation of flax shives results in a general increase of tensile Young's modulus and maximum strength. The Young's modulus increases from + 46% to + 112% when FS-50 and FS-500 respectively are compared to the reference PP-MAPP matrix. FS-500 have a modulus of 3268 (± 240) MPa, which is 90 % that of the FF reinforced composite, and more than a 110% increase in composite rigidity when compared to the WF reinforced PP-MAPP. Moreover, the addition of flax fibres in the FS-500 reinforcing batch does not considerably modify the composite's rigidity.

Furthermore, the composites have an overall dissimilar ultimate strain. FS-250 and FS-500 have a comparable behaviour with small ultimate strains of approximately 2.3% as shown Figure 8a and Table 2. FS-50 and FF+FS-500 both have an ultimate strain 52% higher, while WF and FF exhibit an increase of 109% and 139% respectively given the ultimate strain of the pure matrix of about 11%.

Finally, FS-50 enables a 27% increase in maximum tensile strength when compared to the initial PP-MAPP matrix, while FS-250 and FS-500 have a similar behaviour with values around 25 MPa. When a 50/50 mix of FF and FS-500 is incorporated, a 10% increase in tensile strength is noted, reaching and slightly exceeding that of WF. FS-500 enables the composite to reach almost 80% of the maximum tensile strength of the reference FF reinforced composite. Figure 8b shows that the maximum tensile strength evolves linearly with particle aspect ratio in the composite, highlighting the close relationship between particle morphology and composite tensile strength. Therefore, flax shives have an effective reinforcing potential in PP-MAPP composites and cannot be considered as simply 'fillers' since both the modulus and maximum tensile strength are enhanced compared to the sole matrix.

A comparative graph is shown Figure 9, presenting the mechanical properties of injected polypropylene composites manufactured with a similar process involving an equivalent twin-screw extruder. As mentioned previously, the use of fines obtained either from flax fibres or flax shives (FS-50) increases composite stiffness in a similar manner with a slight advantage for FS-50 which increases composite strength at break by 14%. Wood flour and FS-250 have analogue Young's modulus between 2.8 GPa and 2.9 GPa respectively. Our values of flax fibre reinforced injected composites are in agreement with previous work from the literature.

3.2.3 Role of volume fraction on composite properties

Since FS-500 provides the most efficient mechanical properties among the different shive reinforced batches, it was chosen to investigate the influence of volume fractions on composite mechanical properties. Figure 10 represents the evolution of both the maximum tensile strength and the composite's Young modulus as a function of the volume fraction of FS-500. Young's modulus increases linearly with increasing volume fraction (linear fit with $R^2 = 0.94$), highlighting their reinforcing potential. Furthermore, the maximum tensile strength increases with increasing volume fraction up to about 23%-vol of FS-500 and then decreases above this volume fraction. This behaviour is similar to that of other plant cell wall reinforcing materials, such as flax fibres for which the optimum tensile strength in PP-MAPP injection moulded composites is situated at an optimum volume fraction around 33% [20]. We hypotheses that above this volume fraction, particles become too short to effectively reinforce de polymer matrix, presumably due to increasing shear rates induced by particle-particle friction during processing [61].

The fibre aspect ratio decreases during processing with increasing fibre volume fraction due to increasing induced shear rates [59]. In our case, FS-500 aspect ratio after processing is only 4.8 for the 23%-vol fraction against approximately 20 for the flax fibres used in the study of Ausias et al. [20] for a comparable 20% fibre volume fraction; keeping in mind that in their study the initial fibre length was of 2 mm and that only one step of single-screw extrusion was carried out prior to injection moulding; and this manufacturing process causes fibres to be randomly dispersed in the samples.

3.2.4 Analysis of the critical aspect ratio

When considering a unidirectional composite reinforced by short fibres assumed to be parallel to the applied stress, fibre aspect ratio will influence its tensile strength at break [62]. Assuming that i) the applied load must be transferred to the fibre by the fibre-matrix interface, ii) no loads are transferred at the fibre's section, iii) shear stresses are constant along the fibre's length, iv) the matrix's strain at break is considerably higher than that of the fibres, v) both the matrix and the reinforcing fibres have an elastic and linear behaviour, and vi) the fibres are solid cylinders, Kelly and Tyson established a simplified model [63] defining the critical fibre length L_c as follows (Eq. 3) :

$$L_c = \frac{\sigma_{f,u}\, d}{2\, \tau_i} \qquad \text{Eq. 3}$$

Where $\sigma_{f,u}$ is the ultimate fibre stress, *d* the fibre diameter and τ_i is shear stress at the fibre-matrix interface. The calculation details can be found in different composite literature, by Gibson for instance [62]. The critical aspect ratio can then be considered as the minimal aspect ratio for a fibre to break without pull-out.

SEM images of the fracture surface of PP-MAPP and FS-500 composites (Figure 11) shows that some large particles maintain their alveolar cell structure even after processing, and that the matrix is able to penetrate in it. Furthermore, it even appears that in some places rupture takes place through the flax shive particles due to matrix infiltration (Fig. 11b).

Let us consider FS as a tubular structure in which the elementary volumes, immersed in matrix, have a central lumen completely impregnated by the polymer, as shown in Figure 11b. FS can be simplified as a hollow cylinder having a length L, an average diameter $\bar{d}_f$ and a thickness e. In a similar reasoning as previous, tubes are considered to be parallel to one another in a unidirectional composite. Let's consider d_x, an infinitely small portion of this hollow cylinder along the x axis being fully impregnated with the polymer matrix (as shown in Figure 12), and that the cylinder is parallel to a tensile solicitation of the composite. If we consider, as did Kelly and Tyson, that reinforcing is done in the form of shear stresses considered to be constant along cylinder's length, then the forces applied to the cylinder can be summarized as follows (Eq. 4):

$$(\sigma_{cw} + d\sigma_{cw})S = \sigma_{cw}S + \tau_{i,ins}(\bar{d}_f + e)d_x + \tau_{i,ext}(\bar{d}_f - e)d_x \qquad \text{Eq. 4}$$

With $\sigma_{cw}$the tensile strength applied to the cylinder's surface *S*, τ_e the shear stresses applied on its external surface and τ_i those applied to its inside.

Since the matrix is considered to have an elastic behaviour, then $\tau_{i,ins} = \tau_{i,ext}$, and when resolving this equation based on the Kelly-Tyson model by integration along the cylinder's length, then the previous equation (Eq.4) becomes equation 5, and the critical length at which tensile strength causes cell wall rupture does not depend on fibre diameter (as previously established in equation 3), but rather on the cell wall thickness.

$$L_c = \frac{\sigma_{cw,u} * e}{\tau_i} \qquad \text{Eq. 5}$$

To the best of our knowledge, the average flax xylem cell wall tensile strength has not been reported in the literature. If we consider that flax shives are mainly made of secondary xylem with a composition and structure similar to that of wood, then we can assume that the tensile yield strength of the cell walls of flax shives is also similar to that of gymnosperm earlywood which was measured to be 350 MPa for *Pinus Radiata* [64]. In ongoing studies, we measured the global cell wall thickness in flax xylem to be of 2.4 µm on average by SEM observations of a stem's transverse section. Merotte et al. [65] measured an interfacial shear strength (IFSS) between flax and MAPP of 10.6 ± 2.8 MPa. Therefore, the critical length of a tubular structure assimilated to FS is estimated to be about 79 µm (Eq. 5); against 526 µm estimated using the Kelly-Tyson model (Eq. 3) for a solid-section flax fibre of 15 µm in diameter and an ultimate strength at break of 950 MPa [66]. This is a 6.7 times lower critical length when using this simplistic model, showing the potential reinforcing efficiency of particles which may be considered as fines (less than 200 µm in length) but having a hollow structure, due to the importance of cell wall thickness rather than aspect ratio.

Clearly, in this simplified model the lumen is considered to fully impregnated, and cell wall orientation, matrix wetting and cell wall-matrix adhesion are just a few parameters that might influence shear stresses inside and outside of the tubular cell wall, which may therefore not be equal in reality. Furthermore, cell wall thickness in the xylem evolves with cell wall type, plant maturity and along a flax stem, whereas FS are an assembly of all these different elements creating a gradient in reinforcing potential. Additionally, the assumption that cells are circular is preferred for estimation purposes, but cell wall most often have a polygonal transversal shape that should also be accounted for. This makes FS fragmentation a determining factor for hollow cell accessibility by the matrix.

4. Conclusion

This study focused on the reinforcement potential of flax shives in PP-MAPP injection moulded composites following the investigation of the fragmented by-product materials. The granulometry analysis succeeding raw FS comminution highlights the importance of the mode of particle size analysis which can easily hide small particles or fines. The volume distribution of fragmented flax shives shows that the FS-250 and FS-500 batches are comprised of a high number of particles having a well conserved alveolar structure. Due to the nature of cells, FS have a different biochemical composition than flax fibres as the former contain less than half the latter's amount of cellulose and around six times the latter's amount of lignin. The composition of FS does not evolve with fragmentation, even after an intense attrition-beads milling process. However, the crystallinity index of FS decreases with comminution up to a 50% for the severely transformed FS-50 due to amorphization of particles resulting in a decrease in degree of polymerization and therefore sample crystallinity, as well as a conversion of crystalline cellulose I into cellulose II or III.

Following this preliminary study, the tensile mechanical properties of injection moulded PP-MAPP composites were evaluated. Compounding and injection moulding induced a 70% decrease in flax fibre and FS-250 length but did not modify the length of FS-50 due to their initially small particle size. The tensile maximum strength of the composites increases linearly with particle aspect ratio, and interestingly, FS-500 tensile Young's modulus reaches 90% that of the reference FF composite. The FS-500 sample presented the best mechanical properties among the other fragmented FS batches and was chosen to further analyse the consequences of FS volume fraction. Unlike flax fibres, FS-500 present an optimal tensile strength at 23% in volume fraction, against 33%-vol for flax fibres. SEM observations reveal that the matrix is able to penetrate in some flax shives having a tubular structure. In the case of a hollow cylinder fully impregnated by the matrix, we have shown that the critical length of the particle depends not on particle diameter but rather on tube wall thickness, highlighting the reinforcing potential of hollow fines. The study shows the legitimacy of flax shives as reinforcing material in the field of biocomposites.

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FIGURE CAPTIONS

Figure 1. Reinforcing material length distribution after comminution a) in number, b) in volume. The 10^{th} (first decile), 16^{th}, 50^{th} (median), 84^{th}, and 90^{th} (last decile) percentiles of the cumulative distribution in length are shown respectively from bottom up with corresponding values of 16^{th}, 50^{th} and 84^{th} percentiles facing them.

Figure 2. Length distribution of reinforcing materials and visual aspect as observed with SEM.

Figure 3. Preserved cell wall alveolar structure of some FS-250 particles after comminution. Arrow points to an interesting tracheary element of the flax xylem.

Figure 4. Analysis of lignin, glucose and non-glucosidic monosaccharide content of reinforcing materials.

Figure 5. a) XRD spectra for the ball milled flax shives (raw, 50, 250, 500). For reference, the XRD spectra of Avicel cellulose from Lee et al. [49] marked with * on the graph are also illustrated. b) The evolution in the crystallinity of the samples.

Figure 6. a) Particle length distribution in volume and b) Aspect ratios of extracted materials. The 10th (first decile), 16th, 50th (median), 84th, and 90th (last decile) percentiles of the cumulative distribution in length are shown respectively from bottom up with the 16th, 50th and 84th percentile values facing them.

Figure 7. Screw design of the twin screws used for extrusion, with both transportation areas (white) and kneading areas (grey). Screw length L/D is 40, flow direction is from right to left.

Figure 8. a) Typical tensile stress and deformation behaviour of 30%-wt reinforced PP-MAPP composites, b) Maximum tensile strength of PP-MAPP reinforced composite as function of reinforcing material aspect ratio.

Figure 9. Comparison of mechanical properties provided by different reinforcing materials. For all the batches of this study, both PP-MAPP matrix and extrusion machine are the same. Samples marked with * are obtained from [40].

Figure 10. The Young's modulus and maximum tensile strength of FS-500 reinforced composite as function of volume fraction.

Figure 11. a) Fracture surface of the FS-500 reinforced PP-MAPP composite b) Highlight of a potential matrix penetration in the alveolar structure. Arrows indicate cell-walls.

Figure 12. Schematic representation of the mechanical forces applied to a hollow tubular short cell wall structure in a polymer matrix during tensile testing.

TABLE CAPTIONS

Table 1. Reinforcing material samples and corresponding abbreviations.

Table 2. Tensile properties of injected composites reinforced with 30%-wt reinforcing materials.

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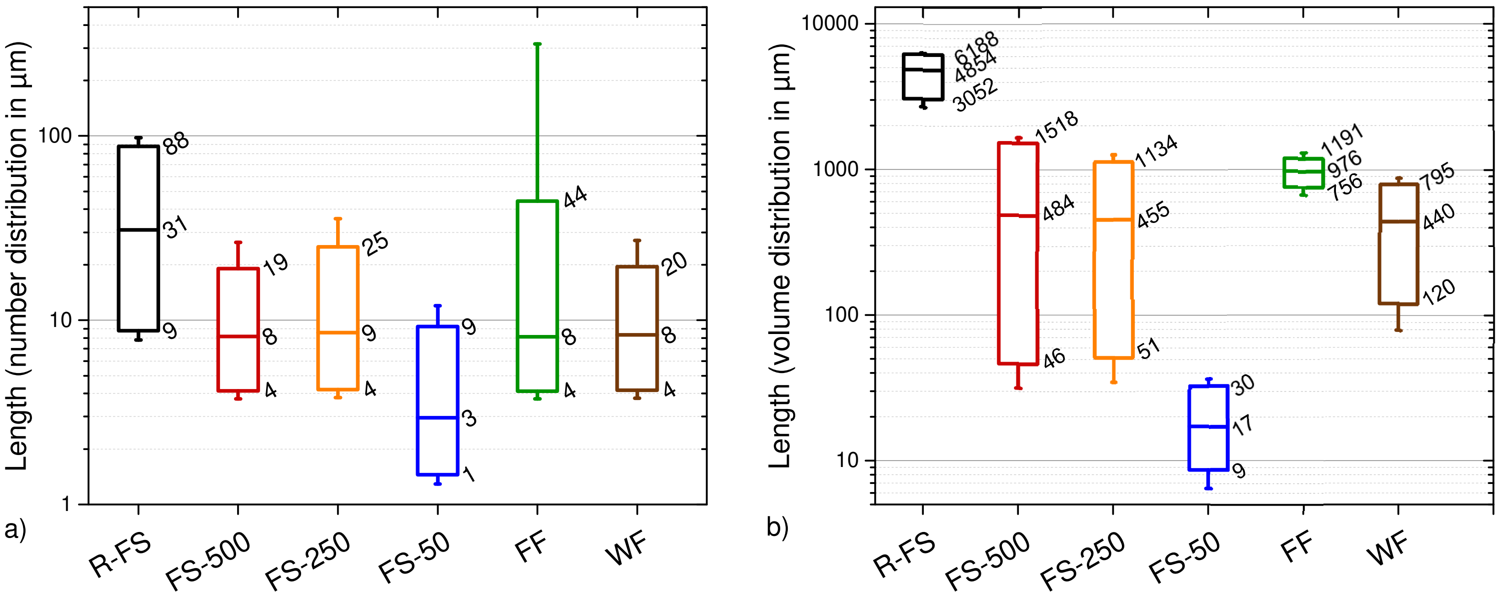

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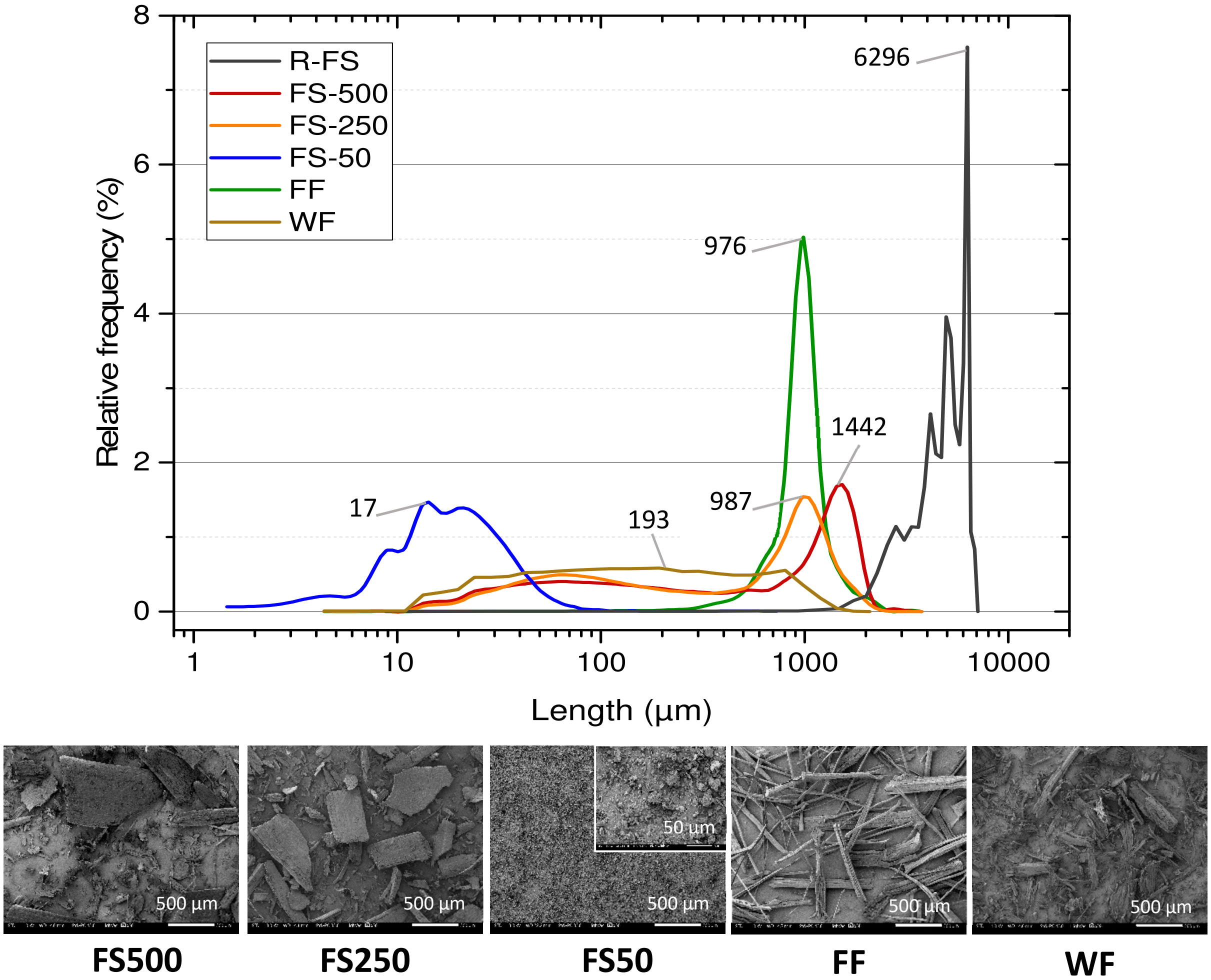

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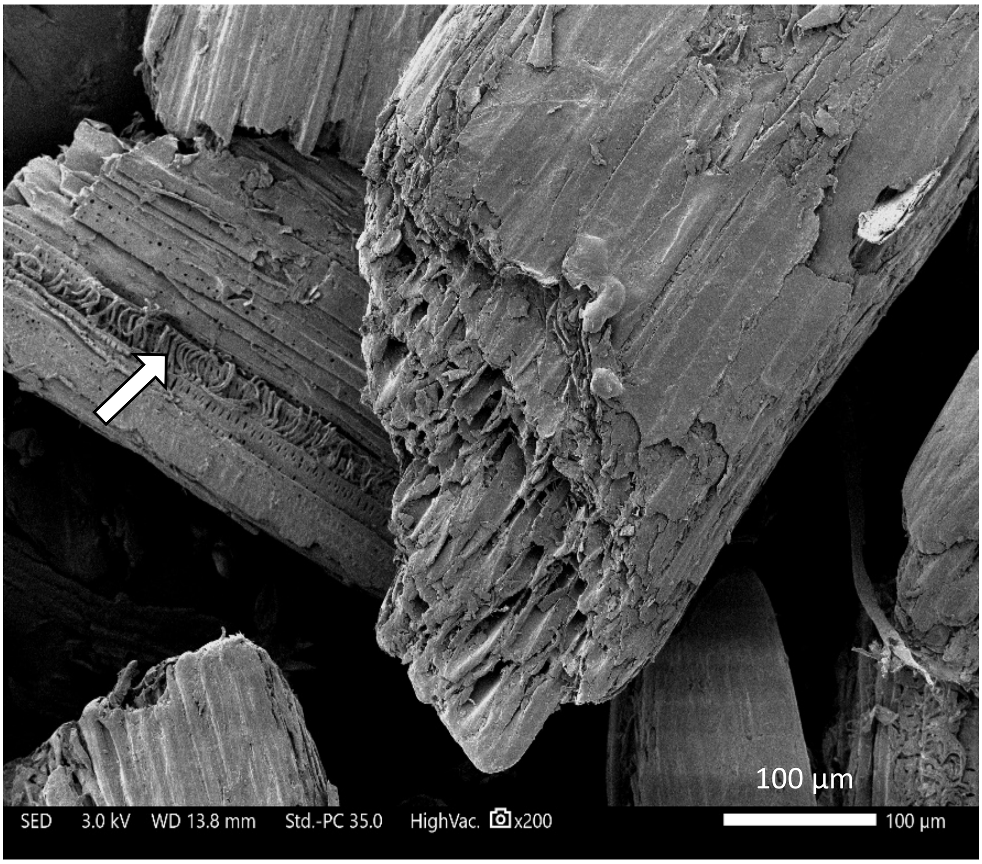

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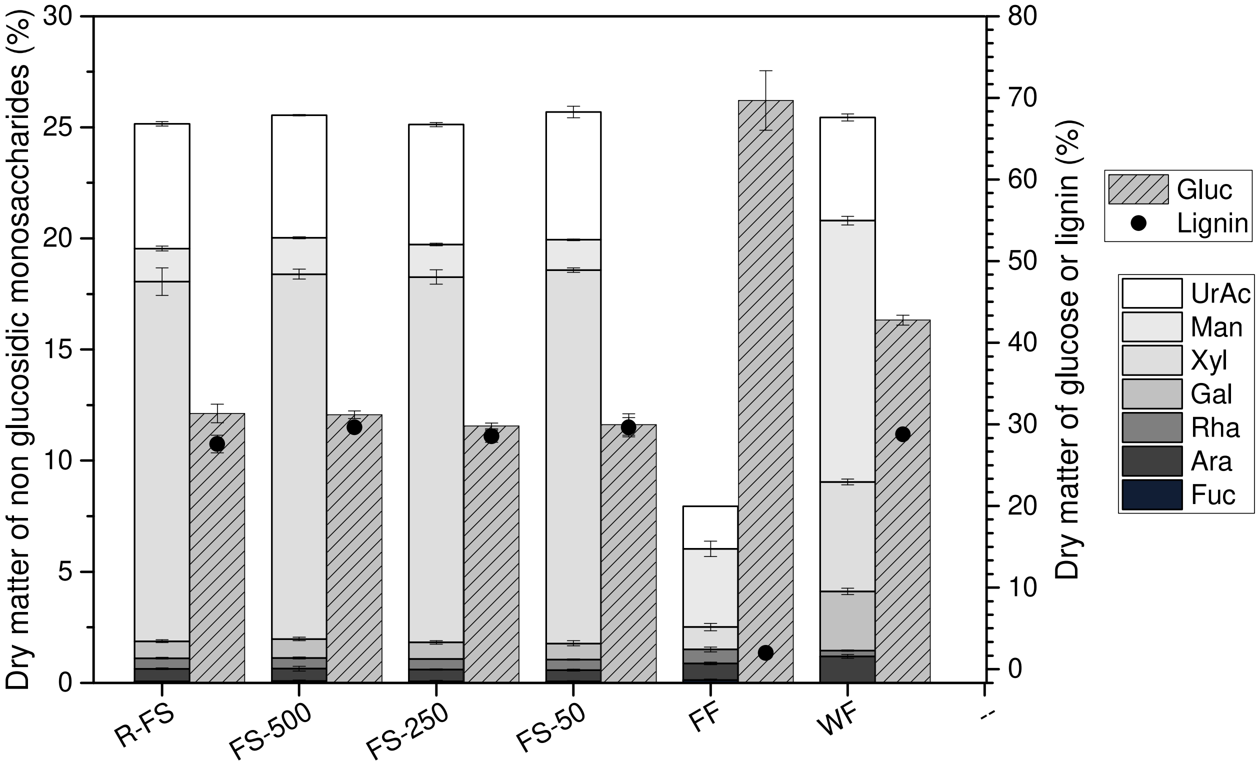

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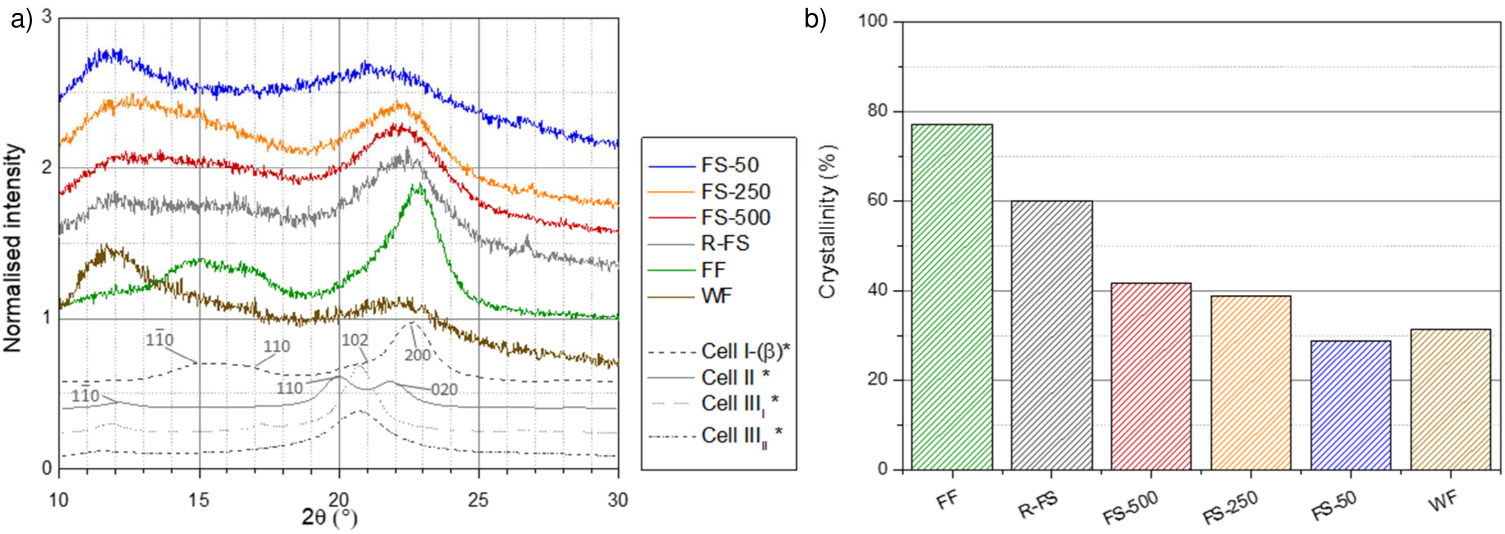

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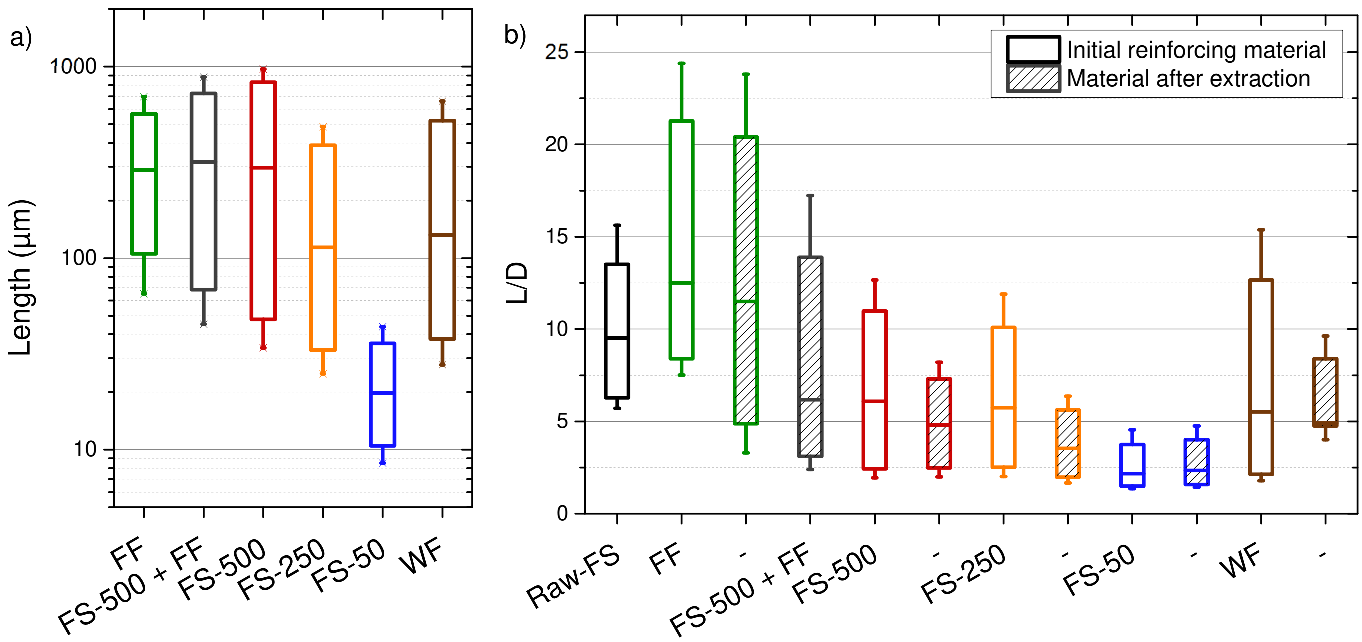
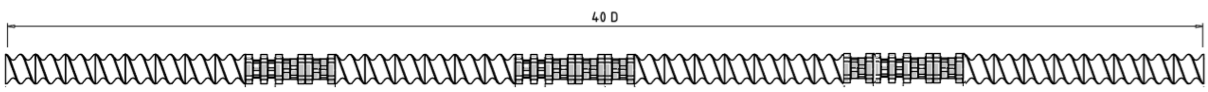


Figure 6. a) Particle length distribution in volume and b) Aspect ratios of initial reinforcing material compared to extracted materials from the 30%-wt reinforced PP-MAPP composite. The 10^{th} (first decile), 16^{th}, 50^{th} (median), 84^{th}, and 90^{th} (last decile) percentiles of the cumulative distribution in length are shown respectively from bottom up.



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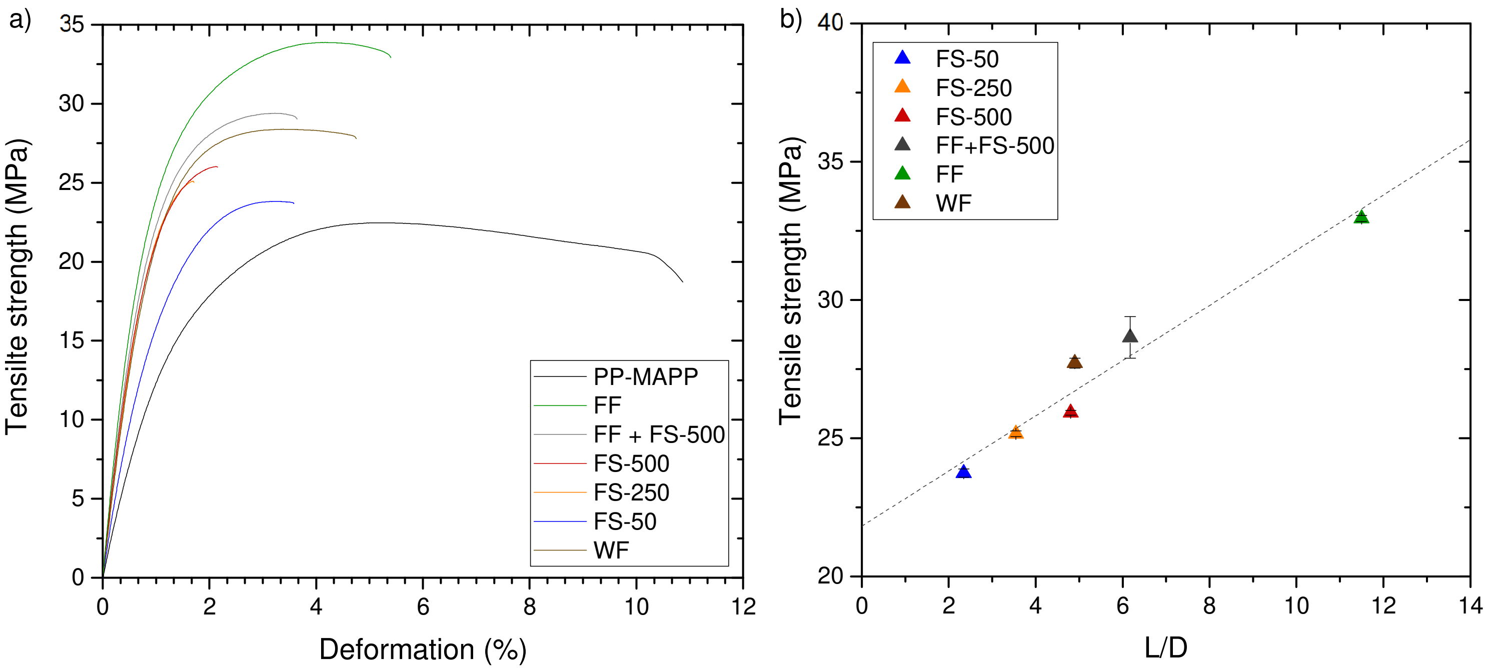

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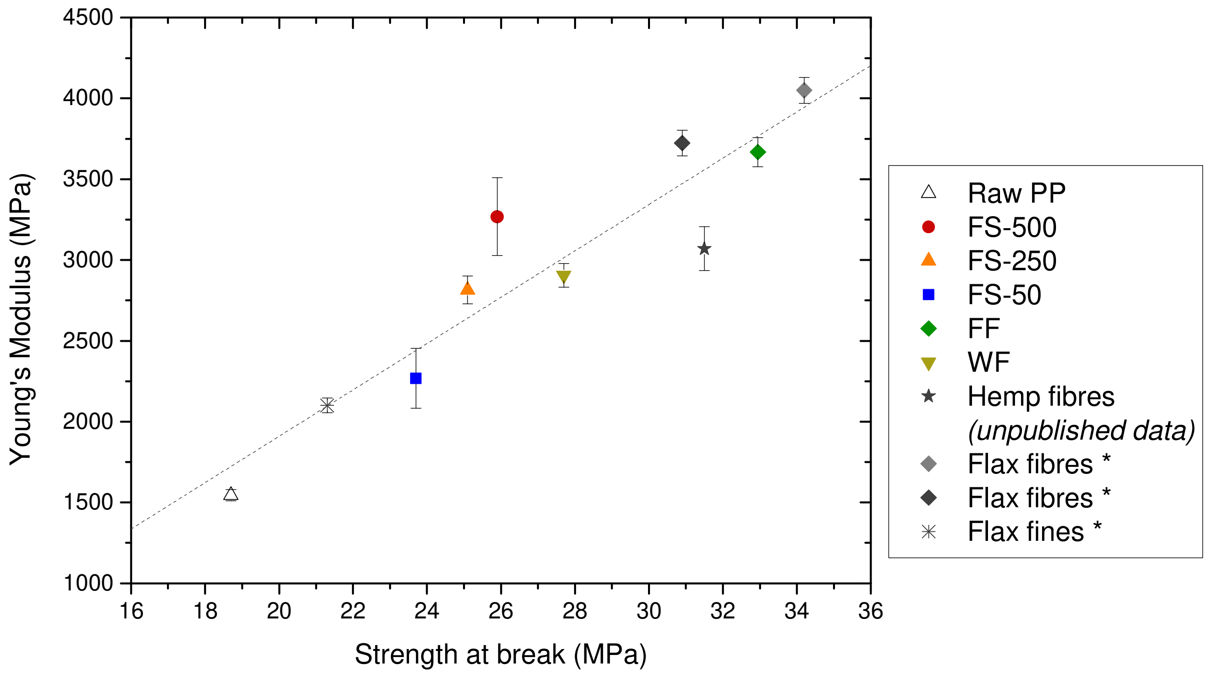

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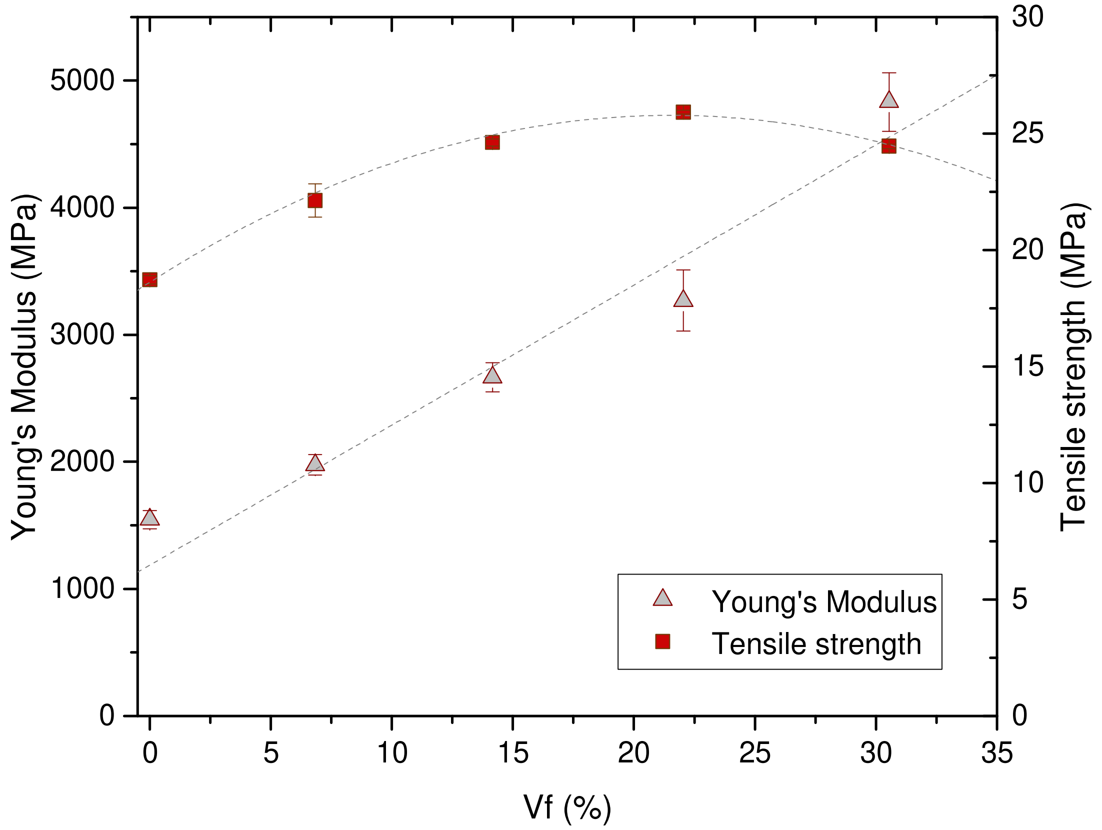

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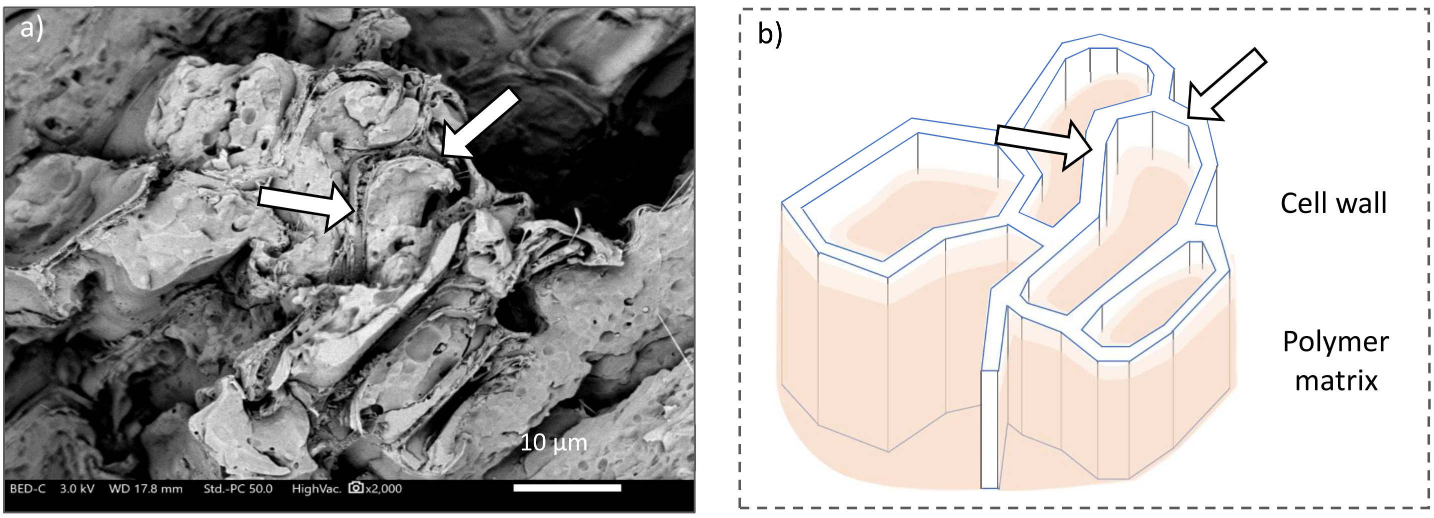

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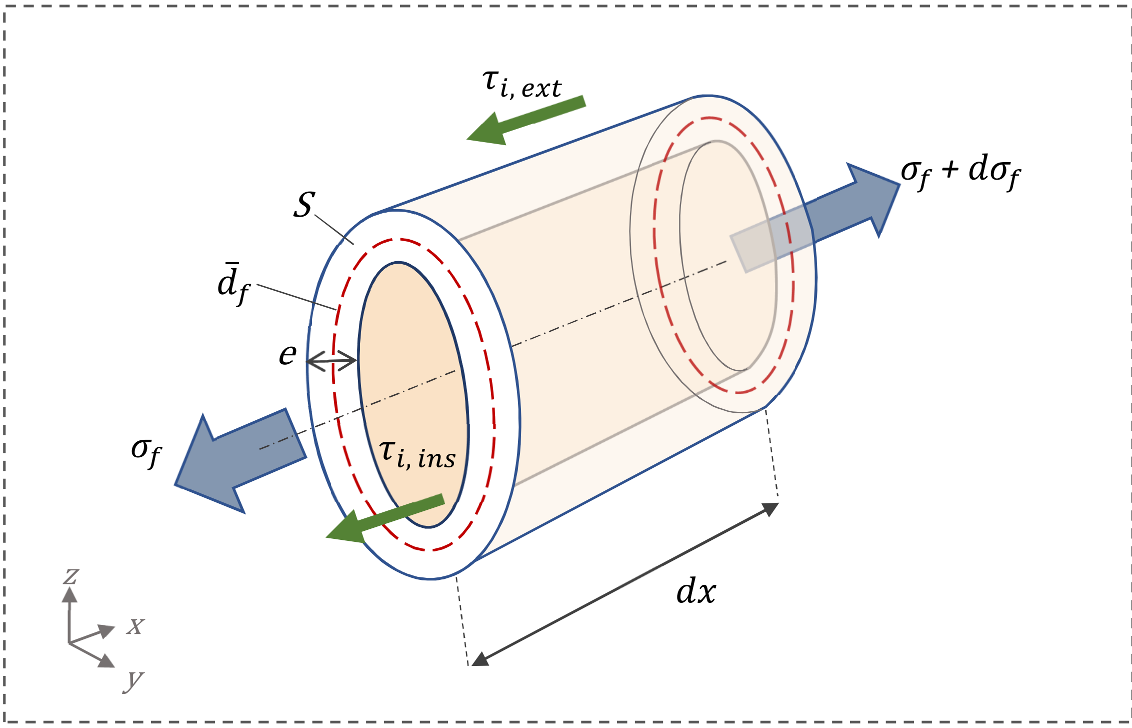

Figure 12. Schematic representation of the mechanical forces applied to a hollow tubular short cell wall structure in a polymer matrix during tensile testing.

Table 1. Reinforcing material samples and corresponding abbreviations.

Sample	Abbreviation	Processing steps
Raw flax shives	R-FS	Obtained from scutching of flax
Flax shives 50	FS-50	Attrition beads milling of R-FS
Flax shives 250	FS-250	Knife milling of R-FS
Flax shives 500	FS-500	Knife milling of R-FS
Flax fibres and flax shives 500	FF + FS-500	50/50-wt mix of FS-500 and FF
Flax fibres	FF	Scutching, hackling and cutting
Wood flour	WF	Fragmentation and sieving

Table 2. Tensile properties of injected composites reinforced with 30%-wt reinforcing materials.

	Young's Modulus *(MPa)*	**Maximum tensile strength** *(MPa)*	**Ultimate strain** *(%)*
PP-MAPP	1545 (± 076)	18.7 (± 0.2)	10.9 (± 0.3)
FS-50	2269 (± 185)	23.7 (± 0.2)	3.4 (± 0.4)
FS-250	2815 (± 086)	25.2 (± 0.1)	2.2 (± 0.6)
FS-500	3268 (± 240)	25.9 (± 0.1)	2.3 (±0.2)
FF + FS-500	3303 (± 083)	28.7 (± 0.8)	3.4 (± 0.7)
FF	3668 (± 090)	33.0 (± 0.1)	5.5 (± 0.2)
WF	2907 (± 073)	27.7 (± 0.2)	4.7 (± 0.1)