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Characterisation of Textile and Oleaginous Flax Fibrous and Shives Material as Potential Reinforcement for Polymer Composites

Lastnosti vlaken in pezdirja iz predivnega in oljnega lana kot potencialnega materiala za ojačitev polimernih kompozitov

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Abstract

In recent years, the use of flax fibres to replace glass fibres as reinforcement in polymer composites has gained popularity due to an increasing environmental concern and requirement for developing sustainable materials. Many works deal with the properties of flax fibres cultivated for textile applications, which are today used for polymer reinforcement. As fibrous material from oleaginous flax varieties and shives is available in large quantities and not promoted, its use in composites shall be further developed in the forthcoming years. Croatia and Slovenia mainly grow oleaginous flax, where after the seed collecting, most of the stems remain unused, the major portion being burned in fields, creating environmental pollution, or being disposed by ploughing. Therefore, the aim of this study was to characterise and compare the properties of shives and technical fibres extracted from flax *Linum usitatissimum* L., a textile variety planted in Croatia and from the Slovenian autochthonous oleaginous variety from Bela Krajina, to be used as potential reinforcement in polymer composites. The flax stems of the textile variety were subjected to water retting for 72 hours and the flax stems of the oleaginous variety were dew retted for four weeks. Dried retted stems were passed through a mechanical process of breaking and scotching, followed by heckling and combing, where the shives and fibres were separated into four groups according to their length. The characterisation of the fibrous material of both varieties was studied according to the results of optical and scanning electron microscopy, moisture regain, fibre length, linear density and tensile strength, and according to the results of Fourier transform infrared spectroscopy and thermogravimetric analysis. Based on the analysis results, it was concluded that the properties of investigated textile and oleaginous flax fibrous material were comparable, as were the properties of tested fibre length groups within the same variety; that flax fibres from textile and oleaginous varieties have adequate morphological and mechanical properties, and thermal stability for reinforcing polymer matrix composites; and that flax shives are more appropriate for fillers in plastics with a lower reinforcing role. As the type of fibre reinforcement (short fibres, roving/yarns, nonwoven or woven fabrics) is very important for polymer composite properties, based on the obtained results, fibres can be selected for specific purposes.
Keywords: textile flax, oleaginous flax, fibrous material, polymer composite, reinforcement

Izvleček

Uporaba lanenih vlaken v zadnjih letih nadomešča uporabo steklenih vlaken za ojačitev polimernih kompozitov zaradi vse večje skrbi za okolje in zahtev za razvoj trajnostnih materialov. Številne raziskave obravnavajo lastnosti

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lanenih vlaken iz predivnega lana, ki se danes uporabljajo za utrjevanje polimerov. Po drugi strani pa se uporabo vlaknatih materialov in pezdirja iz oljnih sort lanu v polimernih kompozitnih ne spodbuja, čeprav so na voljo v velikih količinah. V prihodnjih letih je zato pričakovati razvoj postopkov njihove uporabe v kompozitih. Na Hrvaškem in v Sloveniji gojijo predvsem oljni lan, kjer po odstranitvi semen ostanejo neuporabljena stebla. Večji del stebel sežgejo na polju, kar povzroča onesnaževanje okolja, ali pa stebla zaorjejo. Zato je bil cilj te študije opredeliti in primerjati lastnosti tehničnih vlaken in pezdirja, pridobljenih iz stebel lana Linum usitatissimum L., ki so bila zasajena na Hrvaškem (predivni lan) in v Sloveniji (oljni lan, slovenske avtohtone sorte iz Bele Krajine), z namenom ugotoviti njihovo potencialno uporabnost za ojačitev polimernih kompozitov. Stebla predivne sorte lana so bila godena z namakanjem v vodi 72 ur, stebla oljnega lana pa so bila štiri tedne godena z rosenjem. Iz posušenih godenih stebel, ki so bila v mehanskem postopku trenja na stopah in trlici ter otepanju in česanju (s čimer je bil pezdir ločen od vlaken) izločena vlakna in razvrščena po dolžini v štiri skupine. Lastnosti vlaknatega materiala obeh sort so bile opredeljene na podlagi rezultatov elektronske in optične mikroskopije, vsebnosti vlage, dolžine, finoče, nateznih lastnosti, infrardeče spektroskopije (FT-IR) in termogravimetrične analize. Ugotovljeno je bilo, da so lastnosti vlaken iz predivnega in oljnega lana primerljive, kot tudi lastnosti vlaken v posameznih skupinah v okviru iste sorte; da imajo lanena vlakna iz predivnega in oljnega lana ustrezne morfološke in mehanske lastnosti, kot tudi toplotno stabilnost, ki je potrebna pri izdelavi polimernih kompozitov, in da je pezdir bolj primeren kot polnilo v polimernih kompozitih, kot pa za njihovo ojačitev. Ker je oblika ojačitvenega materiala (kratka vlakna, roving/preje, vlaknovine, tkanine) zelo pomembna za lastnosti polimernega kompozita, je glede na dobljene rezultate mogoče izbrati vlakna za posebne namene.

Ključne besede: predivni lan, oljni lan, vlaknati material, polimerni kompoziti, ojačitev

1 Introduction

Flax is a natural bast fibre that is widely grown in Europe. Furthermore, it is one of the most widely utilised bio-fibres. Two main groups of flax plant *Linum usitatissimum* L. varieties are cultivated – the first for fibre production (textile flax) and the second for linseed oil (oleaginous flax). The harvested area of flax for seed and oil worldwide production is much larger compared to the cultivation of flax for textile applications [1–4].

Flax fibres can be obtained from plants grown primarily for fibre or from waste stems generated in the flax seed production. Textile flax varieties are utilised not only for textile application but also in composites and paper production. Plants for textile varieties grow up to 80–120 cm in height with the stem diameter of about 3 mm, while the plants for oleaginous varieties are smaller, i.e. 60–80 cm in height, and they are thicker [5]. Commercially important flax fibres are historically known by two classes, namely by oriented, long-line fibre for valued linen products and tow (short fibre by-product) for short staple spinning and composites. However, flax stems that are not grown specifically for high value linens may be processed to give a "total fibre" in which a single, non-oriented fibre product results [1]. These fibres can be processed in short staple spinning and nonwoven units. Flax fibres obtained from oleaginous varieties are known as tow (mainly Canadian tow is available on the market) which is usually packed in bales of 136 kg for the shipment to pulp mills for subsequent paper formation. The unused short oleaginous flax stems, which are produced in large quantities around the world, represent an abundant, inexpensive and readily available source of lignocellulosic fibres. After the seed collecting, a major portion of these stems is burned in the field, creating environmental pollution. The exploration of these inexpensive agricultural residues as a bio-source for making industrial products can open new avenues for the utilisation of agricultural residues by reducing the need for disposal and environmental deterioration through pollution, fire and pests, and at the same time add value to the creation of rural agricultural-based economy [1, 3].

Flax fibres can be processed into semi-finished products for the reinforcing of polymer composites. As flax fibres are suitable for different kinds of polymer composite applications, in recent years, the European flax industry has enforced two groups of specially designed flax reinforcement – dry preforms and wet preforms (prepregs), where the full potential of flax can be exploited. Dry preforms consist only of fibres and can be classified as short fibres of specific length or mixed residues, roving/

yarns, nonwoven (mats) and woven reinforcements (UD – unidirectional, 2D – bidirectional and multiaxial). Using these semi-products, the matrix will be added during the composite production. In prepregs, the fibres are already pre-impregnated with the matrix. Pre-impregnated preforms can be classified as compound, thermoplastic and thermoset prepregs (roving/yarn, nonwoven and woven). During the manufacture, the impregnation is completed and the matrix consolidated [3, 6, 7].

The fibre length or its aspect ratio (ratio length-to-diameter) has a great impact on the polymer composite processing techniques [2]. For structural composites (where fibres carry the load), long fibre bundles are required [3]. For short fibre reinforced composites considering the injection and compression moulding techniques, the suggested fibre length is approximately 10 mm and 25 mm (for mats), respectively. For palletising (with matrix), cascade mixing and extruder compounding, the fibre length should be less than 3 mm [2].

The flax fibre is characterised by a very complex structure. When talking about the flax fibre, technical (fibre bundles) and elementary fibres (single plant cells) should be differentiated. Technical fibres (length of up to ~ 1 m, apparent diameter 100–200 μm) separated from the flax plant consist of elementary fibres (length ~ 50 mm, apparent diameter 10–30 μm). The polyhedron-shape elementary fibres overlap one another at a rather large length interval. They are held together by pectin and hemicellulose. The elementary fibres are composed of a very thin (~ 0.2 μm) primary cell wall, a strongly developed secondary cell wall (dominating the cross section) subdivided into three layers, the middle, S2 layer, having the largest dimension, and a lumen, a small, open channel in the centre of the elementary fibre [3, 5, 8]. The secondary cell wall contains crystalline cellulose microfibrils and amorphous hemicellulose. The microfibrils are bundled into mesofibrils that are highly oriented along the fibre axis (at the so-called microfibril angle). Their arrangement in layers is responsible for the mechanical strength and stiffness of the fibre [3, 8].

Flax fibres can be referred to as composites as the cell wall comprises reinforcing oriented semicrystalline cellulose microfibrils which are embedded in a two-phase (lignin-hemicellulose) amorphous matrix [9]. The content of three main polymers (i.e. cellulose, hemicellulose and lignin) is known to vary among plant fibre types. The presence of pectin and waxes can lead to the formation of an ineffective interface between the fibre and polymer matrix with consequent problems such as debonding and

Table 1: Chemical composition of textile and oleaginous flax fibres

Fibre type	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Pectin [%]	Fat and wax [%]	Ash [%]
Textile flax [1]	55.1–75.0	18.6–20.6	2.0–2.2	1.8–2.3	1.7	1.0–2.0
Oleaginous flax [12]	43.0–47.0	24.0–26.0	21.0–23.0	–	–	5.0

Table 2: Influence of fibre properties and characteristics on polymer composite properties [3]

Fibre properties	Composite properties		
	Strength	Young's modulus	Impact resistance
Length ↑	+	≈	++
Diameter ↓	+	+	+
Strength ↑	++	++*	+
Young's modulus ↑	++*	++	––
Elongation ↑	–**	–**	++
Interphase ↑	++	+	–
Dislocation ↑	–	–	––

– decrease, –– strong decrease, + increase, ++strong increase, ≈ low influence

* In general, fibres with high Young's modulus show high strength values and vice versa.

** In general, fibres with higher elongation values show lower strength and Young's modulus values.

voids in resulting composites [1, 9–11]. The chemical composition of textile and oleaginous flax fibres is shown in Table 1.

The reinforcing potential of flax fibres is revealed by the fact that they are high in cellulose content, and that native cellulose has remarkable remarkable tensile stiffness (138 GPa) and strength (> 2 GPa). Flax fibres comprise of around 55–75 wt% cellulose, 53–70% of which is in crystalline form. Therefore, good mechanical properties of flax fibres enable excellent mechanical properties of flax fibre reinforced polymer composites with a high ratio of stiffness to density (fibre density is around 1.5 g/cm^3) [9, 10].

In recent years, the use of flax fibres to replace glass fibres as reinforcement in polymer composites for engineering applications has gained popularity due to an increasing environmental concern and required development of sustainable materials [9]. The performance of flax fibre reinforced composites depends strongly on the properties of used fibres and polymeric matrix, as well as on their ratio, orientation and interface adhesion [13]. A general picture of the influence of flax fibre properties on a polymer composite properties is given in Table 2.

Many works deal with the properties of flax fibres cultivated for textile applications, which are today used for polymer reinforcement. Nevertheless, large quantities of oleaginous flax fibre are obtained each year and are not promoted. The tensile properties of flax fibres are essential when considered as reinforcement in fibre reinforced polymer composites. Pillin et al [14] evaluated the tensile deformation of different oleaginous flax fibres which were cultivated in the same geographic area and lands in a temperate region (Western France). The varieties of oleaginous flax studied were Oliver, Hivernal, Alaska, Niagara and Everest. The used test machine, gauge length and cross-head displacement rate were identical. The results show that interesting mechanical properties were obtained with the oleaginous variety and close to those of textile varieties, e.g. Agatha or Electra. Considering the diameters and specific properties of these elementary oleaginous fibres, it was evidenced that they are good candidates for the substitution of glass fibres in composite materials. The retting degree has no influence on the diameters and mechanical properties of fibres. The same conclusion is obtained with agronomic factors such as seeding rate and plant height. In the study by Baley and Bourmaud [15], the fibre tensile properties of 50 batches of 14 textile and oleaginous flax (*Linum usitatissimum* L.) varieties cultivated in France (Normandy) between 1993 and 2011 were compared. Their varietal and geographical origins were known and the tensile test conditions were similar. Contrary to the widespread idea, the stiffness of elementary textile flax fibres was very close to that of oleaginous flax fibres (Young's modulus 52.4 GPa vs. 52.8 GPa), whereas their breakage properties were slightly better (tensile strength 976 MPa vs. 855 MPa and elongation at break 2.15% vs. 1.82%). The results show a strong performance of oleaginous flax fibres and justify their use as reinforcement for polymers. A detailed analysis of the results does not show any important impact of the variety nor the cultivation year. There was no very weak batch with poor mechanical properties. It was concluded that by using a blend of batches, it is possible to guarantee specific mechanical properties that can compete with those of glass fibres. Moreover, it should be highlighted that all tensile properties are widely scattered [2, 15–18]; this phenomenon also occurred at the breakage properties of glass fibres in opposition to their Young's modulus, which is more stable [15]. Fuqua et al [19] assessed the property variation between polymer matrix composites unidirectionally reinforced with dew retted, finely combed, long-line flax fibre versus randomly oriented polymer composite reinforced with combine harvested, minimally retted, short oleaginous flax fibre with high percentage of shives. Varieties, farming conditions, harvest and processing of flax impact the manufacturability of flax fibre reinforced composites. The flax fibre bundle pull-out tests proved that with appropriate cleaning, orientation and combing, similar composite properties were obtained from samples. In a study by Mekic et al [20], the oleaginous flax fibre was investigated for its composite processability as compared to traditional fibreglass. The studied liquid flow through flax fibre performs was similar to the fibreglass performs with the same porosity values under identical processing conditions.

Despite the use of non-wood and non-cotton plant fibres in reinforced plastics having tripled to 45,000 tonnes over the last decade, plant fibre reinforced composites make up only around 1.9% of the 2.4 million tonnes of the EU fibre reinforced composite market, primarily flax (64% of the market

share). It is forecasted that about 830,000 tonnes of bio-fibres will be consumed by 2020 and that the share will go up to 28% of the total reinforcement materials [2, 3, 5]. It should be noted that the harvested area of oleaginous flax varieties displays a considerable quantity of short oleaginous flax fibres. As fibrous materials from oleaginous flax varieties and shives are available in large quantities, their use in composites shall be further developed in the forthcoming years. Moreover, the processing technique for oleaginous flax fibres needs to be adapted and optimised to develop alternative fibre supply sources for the composite industry. In Croatia and Slovenia, mainly oleaginous flax is grown, where after the seed collecting, most of the stems remain unused and a major portion is burned in the field, creating environmental pollution or is disposed by ploughing. Therefore, the aim of this study was to characterise and compare the properties of shives and technical fibres extracted from the flax *Linum usitatissimum* L. textile variety planted in Croatia and from the Slovenian autochthonous oleaginous variety from Bela Krajina, to define if they can be used as potential reinforcement in polymer composites.

2 Materials and methods

2.1 Materials

The following technical flax fibres were used in this study:

a) Textile flax (variety Viola, Van de Bilt Zaden, Netherlands) planted in 2009 in Križevci in Croatia. Flax was manually harvested in the phase of early yellow maturity in late June. Flax stems were subjected to water retting for 72 hours in a laboratory tank with tap water heated to the temperature of 32 °C.
b) Oleaginous flax (Slovenian autochthonous variety from Bela Krajina) planted in 2010 in Slovenia on an experimental field of the Biotechnical Faculty, University of Ljubljana, Slovenia. Oleaginous flax was manually harvested in the phase of yellow maturity in early July. Flax stems were laid on the soil for dew retting for four weeks.

After the retting and drying, the stems were passed through a mechanical process of breaking and scotching. The next step was heckling and combing of flax to align fibres removing neps, dust and extraneous matters whereby fibres and shives were

Figure 1: Cleaning, orientation and combing of textile flax technical fibres, and separated shives

Figure 2: Cleaning, orientation and combing of oleaginous flax technical fibres

separated. With regard to the length, the fibres were additionally separated into four length groups – from longer to shorter fibres (Figures 1 and 2).

2.2 Methods

Mechanical properties, chemical composition, physical and morphological properties, thermal stability during processing and use, hygroscopic behaviour and fibre/matrix adhesion are important factors in determining the performance properties of a fibrous material if used as reinforcement in polymer composites. Therefore, a characterisation of the fibrous material of both varieties was studied with:

a) Optical and Scanning Electron Microscopy (SEM). The longitudinal and cross-sectional views of flax fibres of both varieties were taken by using an Olympus CH20 optical microscope and Dino microscope eye-piece camera. The surface morphology of flax fibres and shives was examined with a SEM analysis using JEOL 6060 LV SEM, Japan (at the accelerating voltage of 10 kV). For SEM analyses, the samples were previously coated with a gold/palladium admixture to the extent of 90/10% in sputter coater.
b) Moisture regain. The moisture content in fibres (for each length group) and shives was determined according to ASTM D 2654-89a [21]. The specimens were conditioned in a standard atmosphere (temperature of 20 ± 2 °C and relative humidity of 65 ± 4%) for 24 h, weighed, dried in an oven at the temperature of 105 °C and reweighed. The difference between the mass of conditioned and the mass of oven-dried samples was calculated as moisture regain and expressed in percentage.
c) *Length* of individual flax fibres. For each length group of technical fibres, the length was determined according to ISO 6989 [22], method A: on a straightened fibre on a graduated rule, under a light tension applied with the aid of forceps and grease.
d) Linear density of individual flax fibres. For each length group of technical fibres, linear density was examined according to EN ISO 1973 [23], using Vibroscop 400, Lenzing. Both, linear density and tensile properties were determined for the same fibres.
e) Tensile properties of individual flax fibres. Using gauge length, shorter than the length of a single fibre cell, the properties of the cell wall in technical fibres were measured. Breaking force, breaking elongation, tensile strength and Young's modulus for each length group of technical fibres were determined according to EN ISO 5079 [24], using Vibrodin 400, Lenzing, with cogged steel clamps at the following conditions – gauge length: 5 mm, elongation rate: 3 mm/min, pretension: 1500 mg.

   The fibre specimens for testing the length, linear density and tensile properties were conditioned in standard atmosphere. The average values ($\bar{x}$) of 100 measurements and their coefficient of variation (CV) were calculated. The number of measurements was adapted according to the statistical indications of the degree of reliability with 95% confidence interval. As the diameter and tensile properties of a flax fibre are not uniform along its length [2], the linear density and tensile properties of fibres were determined on a fibre section (60 mm in length) that was taken in the middle of each fibre bundle of a certain length group.
f) *Fourier transform infrared (FT-IR) spectroscopy*. The FT-IR spectra of shives and technical flax fibres of both varieties were obtained with a Perkin Elmer Spectrum 100 FT-IR spectrometer,

using the non-destructive attenuated total-reflection (ATR) method. The results are collected from a region between the surface and depth of about 0.5–5.0 μm, depending on sample characteristics [25, 26]. All spectra were recorded over the range of 4000 cm^{-1} to 380 cm^{-1}, with the resolution of 4 cm^{-1} and 8 scans. The spectra were normalised to the absorption band at 1312 cm^{-1}. All samples for the FT-IR spectroscopy were prepared in the same standard conditions, which enabled the crystallinity index of cellulose to be evaluated using the obtained spectra. The index I_c is determined as the ratio of intensities of absorption bands at 1368 and 2918 cm^{-1}, I_{1368} and I_{2918}, respectively [27]:

$$I_c = I_{1368}/I_{2918} \quad (1)$$

g) Thermogravimetric analysis (TGA). TGA is an analytical technique used to determine the thermal stability of a material by monitoring the weight change that occurs when a sample is heated at a constant rate (non-isothermal thermogravimetry) in a controlled atmosphere. As the thermal stability of a fibrous flax material at a higher temperature is one of the most important factors during the processing of polymer composites (especially thermoplastic), a Perkin Elmer Pyris 1 thermogravimetric analyser was used for the thermal degradation of technical flax fibres and shives as well as for the determination of their thermal stability. The weight of all analysed samples was 7.0 ± 1.0 mg. The analysis was performed in a nitrogen atmosphere with the flow rate 30 ml/min, temperature range from 50 to 700 °C and 10 °C/min heating rate to avoid the unwanted oxidation.

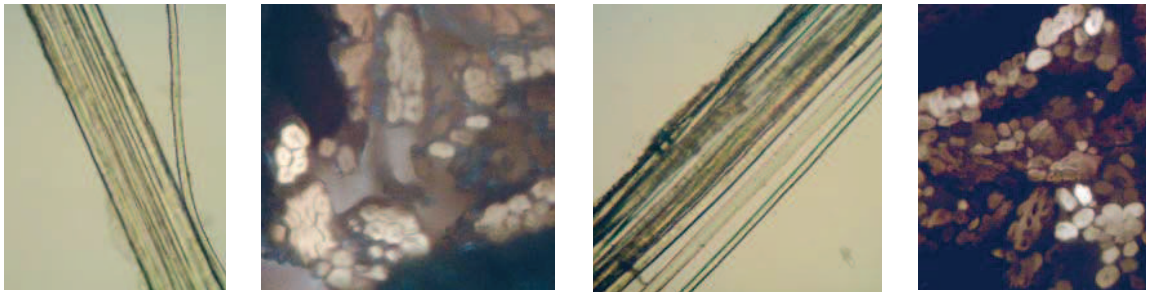
3 Results and discussion

3.1 Optical and SEM microscopy

The optical and SEM micrographs of textile and oleaginous flax fibres for all tested length groups are very similar. Figure 3 shows the longitudinal and cross-sectional optical views of flax fibres of both varieties. It is clearly seen that the surface impurities and non-cellulosic materials are present on the surface of flax fibres (Figures 3a and 3c). Both types of fibres have kink bands that appear as horizontal bands in elementary fibres. It is confirmed that the flax fibres of both varieties exist as a bundle of elementary fibres of polygonal cross-sectional shape, which can vary in their dimensions (Figures 3b and 3d).

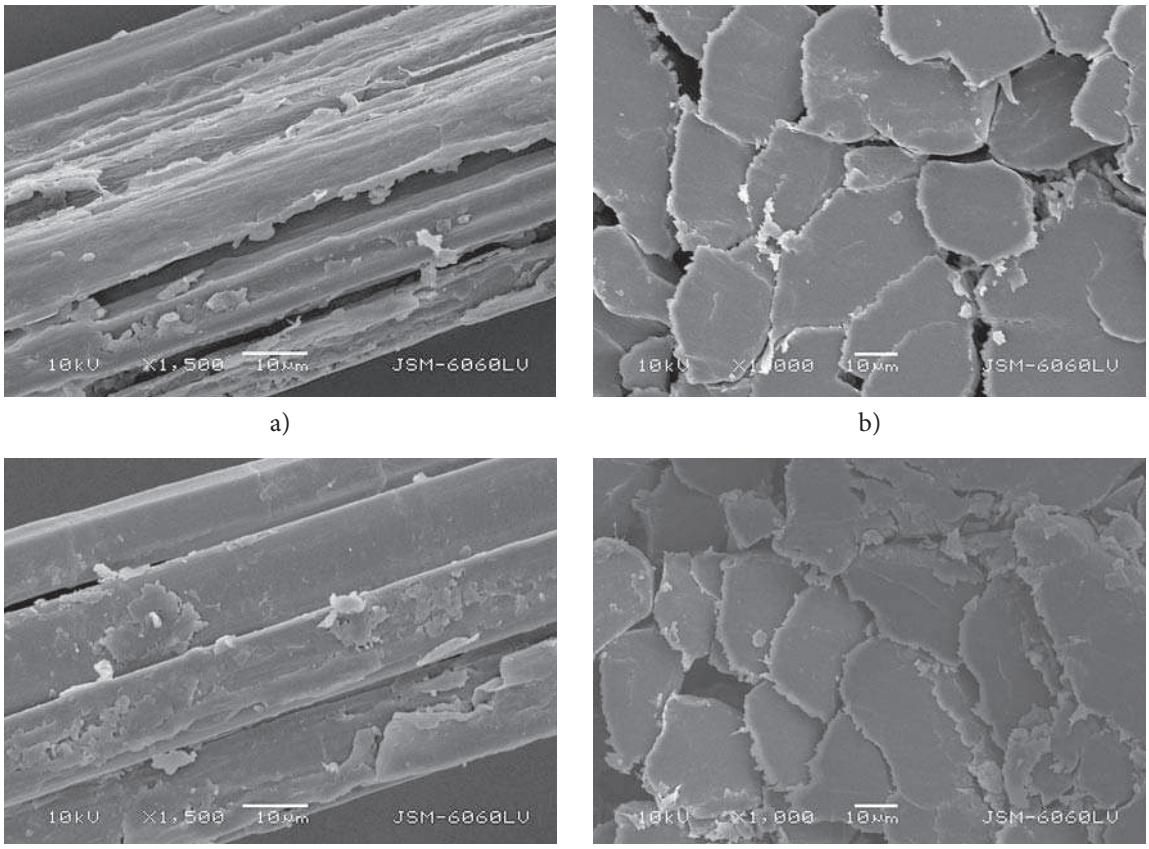
The surface morphology of fibres and shives was studied using the scanning electron microscopic analysis. The SEM micrographs of the fibre surface and fibre cross-section for both varieties are given in Figure 4. Figures 4a and 4c confirm that the structure of flax fibres includes several elementary fibres bonded along the fibre axis, as well as the presence of surface pectin material, which is also determined in optical images. The cross-section of fibres (Figures 4b and 4d) indicates the presence of a thick secondary wall.

The diameter of elementary fibres of both varieties is very similar, as it is shown in Figure 4. The diameter values of textile flax elementary fibres measured in the cross-section of 100 fibres that exist in bundles vary from 8.79–30.90 μm and for oleaginous flax fibres from 10.10–34.00 μm. The average diameter of elementary textile flax fibres was roughly measured as 18.92 μm (with corresponding coefficient of variation CV = 27.32%) and for oleaginous flax fibres as 20.95 μm (CV = 31.07%).



a) b) c) d)

Figure 3: Optical microscopy images of flax fibres: longitudinal views (magnification 100×) and cross-sectional views (magnification 200×) of textile flax fibres (a, b) and oleaginous flax fibres (c, d)

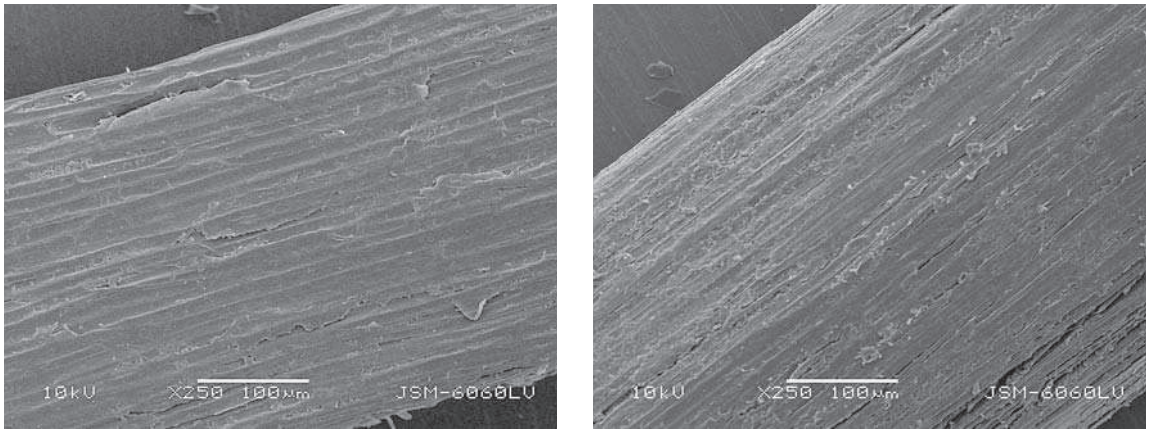


a) b)

c) d)

Figure 4: SEM micrographs of flax fibres: longitudinal views (magnification 1500×) and cross-sectional views (magnification 1000×) of textile (a, b) and oleaginous flax fibres (c, d)

Flax fibres were extracted from phloem, which surrounded them in flax plants and occurred in bundles under epidermis. Xylem material (woody core or shives) is located in the middle part of the plant [5]. The surface morphology of shives is very similar for both varieties and is given in Figure 5.



a) b)

Figure 5: SEM micrographs of shives: longitudinal views (magnification 250×) of textile (a) and oleaginous flax (b)

3.2 Moisture regain

The moisture content of flax fibrous material is one of the most important criteria which has to be considered in choosing the reinforcement material. Moisture content affects the dimensional stability, electrical resistivity, tensile strength, porosity and swelling behaviour of flax fibres in polymer composites. The chemical composition and location of constituents define the sorption properties of a flax fibrous material. Cellulose is a semicrystalline polysaccharide with a large amount of hydroxyl groups, giving flax fibres their hydrophilic nature. When they are used to reinforce hydrophobic matrices, the adhesion between them is low and is accompanied by poor resistance to moisture absorption. Hemicelluloses are strongly bonded to cellulose fibrils presumably by hydrogen bonds. Hemicellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Due to their open structure, containing mainly hydroxyl and acetyl groups, hemicelluloses are hygroscopic and are partially soluble in water. Lignin and pectin act mainly as bonding agents. Lignin is more hydrophobic and composed of amorphous, highly complex, mainly aromatic, polymers of phenyl-propane units. The waxy substances of flax fibres affect the lower fibre wettability and adhesion characteristics [2, 26].

The moisture regain of tested technical fibres of textile flax was in the range from 9.73% to 9.35% and for oleaginous flax fibres in the range from 9.14% to 8.89%, as it can be seen in Figure 6. The moisture regain of textile flax shives (TFS) was 10.38% and for oleaginous flax shives (OFS) 9.54%. The highest values were obtained for the shives and the longest fibres (TF1 and OF1) of both varieties. The textile flax fibre moisture regain is slightly higher than that of oleaginous fibres, which indicates a slight difference in the chemical composition of fibres (Table 1).

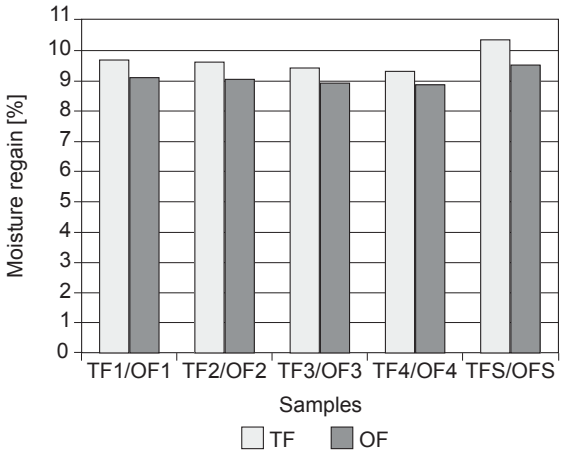


Figure 6: Moisture regain of flax fibrous material – technical fibres of textile flax separated into four length groups (TF1–TF4) and shives (TFS); and technical fibres of oleaginous flax separated into four length groups (OF1–OF4) and shives (OFS)

3.3 Fibre length, linear density and tensile properties

The results of average values of fibre length and linear density obtained on technical textile (TF) and oleaginous (OF) flax fibres, alongside with the corresponding coefficient of variation are presented in Figures 7 and 8.

During the fibre samples preparation, a smaller proportion of longer fibres was determined at oleaginous flax fibres than at textile flax fibres. By comparing the results of length and linear density of technical flax fibres from textile and oleaginous flax, it was established that:

- Flax fibres obtained from textile flax are on average longer than flax fibres obtained from oleaginous flax (Figure 7). Average length of two longer fibre groups 1 and 2 is higher in textile flax fibres (TF1, 337.5 mm; TF2, 201.6 mm vs. OF1, 260.6 mm; OF2, 132.2 mm).
- Although the technical fibre linear density depends on the shape and length of elementary fibres, their number in the fibre bundle to be evaluated, the flax variety and processing method [3], it was found out that the differences in the fibre linear density between the length groups of textile flax variety (TF1–TF4) are minimal (39.47– 37.35 dtex). In case of oleaginous flax, the longest fibres (OF1, 260 mm) are also the finest fibres (29.97 dtex). Shorter oleaginous flax fibres (OF2–OF4) have higher linear density (39.59– 34.75 dtex), comparable with textile flax fibres (Figure 8).
- A relatively large coefficient of variation is found for flax fibres within the length groups, even for the same variety, which indicates highly variable properties. The variability is more pronounced in textile flax fibres (Figures 7 and 8).

The results of average values of fibre tensile properties obtained on technical textile (TF) and oleaginous (OF) flax fibres, together with the corresponding coefficient of variation are presented in Table 3.

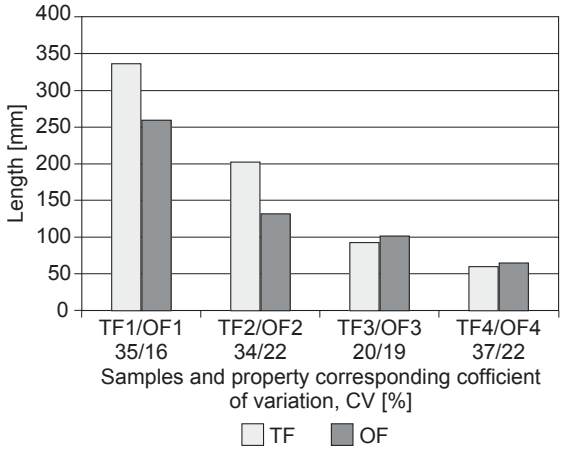


Figure 7: Average length of flax technical fibres separated into four length groups – textile flax (TF1–TF4) and oleaginous flax (OF1–OF4)

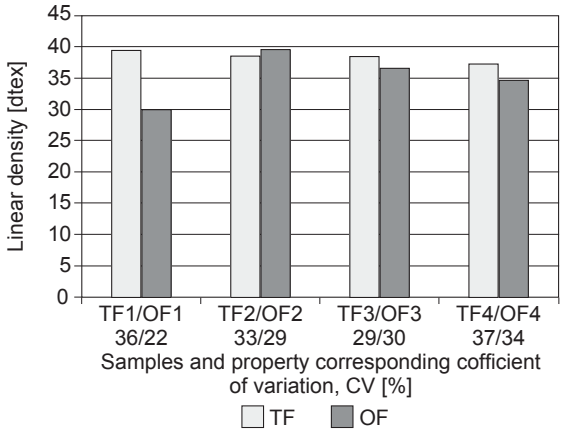


Figure 8: Average linear density of flax technical fibres separated into four length groups – textile flax (TF1–TF4) and oleaginous flax (OF1–OF4)

Studies by Romhány et al [8] showed that there are three failure mechanisms of technical flax fibres: 1) longitudinal splitting of the pectin boundary layer among elementary fibres; 2) transverse fracture of elementary fibres; and 3) multiple fractures of elementary fibres and their microfibrils. Generally, a higher tensile strength is observed for fibres with shorter test gauge length. The reasons are two-fold: firstly, the longer the fibre, the higher the probability of containing weak links or imperfections (e.g. kink bands), and secondly, the failure mechanism of technical fibres at shorter clamping length is different from that at longer clamping length. At large clamping length, flax fibre failure takes place through the relatively weak pectin interphase that bonds the elementary fibres together. The pectin interphase is oriented predominantly in the length direction of the fibre, it breaks by shear failure. At clamping length below the elementary fibre length, usually stronger cellulosic cell wall of elementary fibres is loaded [2, 28].

The dispersion of tensile properties is due to the variation in the cellulose, lignin and pectin content which is different from one fibre to another, and also due to the randomness of the location and size of defects in the stressed fibre segment. Therefore, a relatively high CV for tensile properties was established for technical fibres (Table 3), even low gauge length of 5 mm was selected for measurements. By comparing the tensile properties of technical fibres from textile and oleaginous flax separated into four length groups, it was established that with the reduction in fibre length, the values of breaking force, tensile strength and breaking elongation decrease,

Table 3: Tensile properties of flax technical fibres separated into four length groups – textile flax (TF1–TF4) and oleaginous flax (OF1–OF4)

Sample	Breaking force		Tensile strength		Breaking elongation		Young's modulus	
	$\bar{x}$ [cN]	*CV* [%]	$\bar{x}$ [cN/tex]	*CV* [%]	$\bar{x}$ [%]	*CV* [%]	$\bar{x}$ [cN/dtex]	*CV* [%]
TF1	241.74	35.67	64.13	37.30	3.87	30.50	173.72	34.60
TF2	214.12	38.90	57.01	31.53	3.77	29.03	159.52	31.71
TF3	183.02	43.08	48.57	37.76	3.49	31.77	137.83	33.41
TF4	169.92	50.43	46.43	39.71	3.26	33.60	136.52	34.71
OF1	195.58	31.78	66.19	28.15	3.25	21.13	204.42	19.91
OF2	209.01	36.65	54.47	36.83	3.52	24.11	145.44	26.65
OF3	187.37	38.39	53.93	42.18	3.24	26.41	155.96	34.61
OF4	171.73	50.43	49.52	36.44	2.92	29.05	170.41	31.22

increasing the dispersion of measurement results. The tensile strength values of two flax varieties are comparable. However, it was found out that the longest and the finest oleaginous flax fibres (OF1, 260 mm) are also the strongest (tensile strength 66.19 cN/tex). The values of oleaginous flax fibre breaking elongation are minimally lower (OF, 3.52–2.92%) than at textile flax (TF, 3.87– 3.26%) which is in accordance with the published data [15].

With cellulose microfibrils spiral angle (MFA) of 6 to 10° in cell fibres, flax fibres are among the plant fibres with higher tenacity [3]. The tensile strength values obtained by investigation are high and also within the range of published data (2.6–7.7 g/den) [1]. The Young's modulus of fibres is governed by the increase of cellulose content and decrease of MFA [3]. Although the values of the Young's modulus are higher for the flax fibres obtained from oleaginous flax, the relatively high Young's modulus is determined for both varieties – the highest for longer fibres (OF1, 204.42 vs. TF1, 173.72).

3.4 FT-IR analysis

The lignocellulosic fibrous material compounds containing cellulose, hemicelluloses and lignin consist of oxygen containing functional groups (ester, ketone and alcohol), alkenes and aromatic groups [1, 11, 25, 26, 29, 30]. The Fourier transform infrared (FT-IR) spectra of flax fibres separated into four length groups and shives are shown in Figures 9 and 10. The FT-IR spectra of textile (Figure 9) and oleaginous flax (Figure 10) fibres for all tested length groups are very similar, with no significant differences. The spectra of shives are somewhat different compared to the spectra of flax fibres, namely according to the intensity of identified bands in the spectra.

As shown in Figures 9 and 10, for all fibre length groups, a broad absorption band was observed at 3333 cm^{-1} (TF) and 3336 cm^{-1} (OF) due to the OH stretching in H-bonded hydroxyls groups of cellulose and hemicelluloses (characteristic band position for H-bonded hydroxyl groups is between 3200–3400 cm^{-1}). In shives, this band was observed at 3331 cm^{-1} for TFS and at 3337 cm^{-1} for OFS, respectively. The absorption bands at 2918 cm^{-1} and at 2850 cm^{-1} correspond to the C−H symmetrical stretching vibration and C−H symmetrical stretching vibration from CH_2 in cellulose and hemicelluloses. The C=O stretching vibration of the linkage of carboxylic acid in lignin or ester group in hemicelluloses is centred at 1734 cm^{-1} (characteristic band position is between 1720–1740 cm^{-1}, more precisely between 1731–1734 cm^{-1}). The band at 1632 cm^{-1} (TF) and 1641 cm^{-1} (OF) is assigned to the OH bending of physically adsorbed water molecules in noncrystalline cellulose (characteristic band position is 1625–1660 cm^{-1}). In the spectra of shives, it appears at 1645 cm^{-1}. The C=C stretching of the aromatic skeleton ring of lignin appears at around 1515 cm^{-1}. The same band at 1513 cm^{-1}, present in the spectra of shives and elsewhere only as a weak shoulder, confirms the lower content of lignin in all flax fibres. The band at 1425 cm^{-1} corresponds to C−H in plane bending deformation connected with the methoxyl group in lignin and is present in all flax fibre spectra (characteristic band position is between 1400–1430 cm^{-1}). In the spectra of shives, it appears at 1423 cm^{-1}, where an additional band at 1463 cm^{-1} corresponds to the asymmetrical C−H bending in the CH_2 and OH deformation that is also present in the spectra of OL2-OL4 oleaginous fibres (characteristic band position is between 1450–1475 cm^{-1}). The bands around 1370 cm^{-1} correspond to the in-plane CH bending form CH_2 in cellulose and hemicelluloses. In the fibre spectra, this band appears at 1368 cm^{-1} and in shives, at 1373 cm^{-1}. The band at 1202 cm^{-1} corresponds to the C−O−C symmetrical stretching in cellulose and hemicelluloses. It is present in all flax fibre spectra and only as a weak shoulder in the spectra of flax shives. The band at 1247 cm^{-1} may be attributed to the Guaiacyl ring breathing with the C−O stretching and is characteristic of lignin (band position is around 1250 cm^{-1}). It is clearly present in the spectra of shorter flax fibres (TF2-4 and OF2-4) and only as a shoulder in the spectra of the long flax fibres of both varieties. In the shives spectra, it is present as a very intensive band at 1242 cm^{-1} that corresponds to the C−O bond of the acetyl group in xylan and hemicelluloses. The band detected at 1156 cm^{-1} in all spectra (characteristic band position is between 1150–1160 cm^{-1}) corresponds to the asymmetrical stretching deformation of the C−O−C band in cellulose. The β-glycosidic linkages between monosaccharides show a band at 896 cm^{-1} in all spectra (asymmetrical stretching owing to β linkage in cellulose is characteristic of 890–900 cm^{-1}). The band at 660 cm^{-1} corresponds to the C−OH out-of-plane bending in cellulose and is present in all flax fibre spectra. In

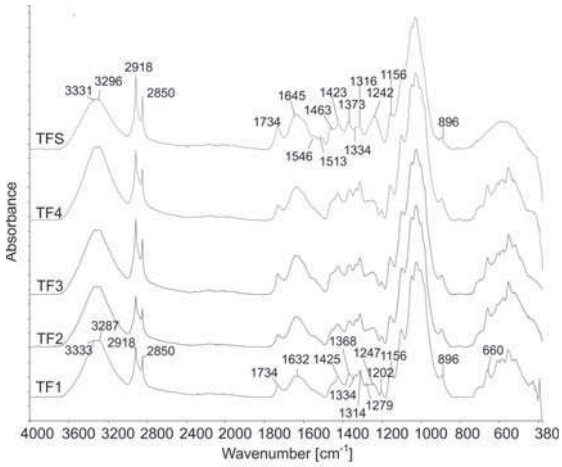


Figure 9: FT-IR spectra of textile flax fibres separated into four length groups (TF1–TF4) and shives (TFS)

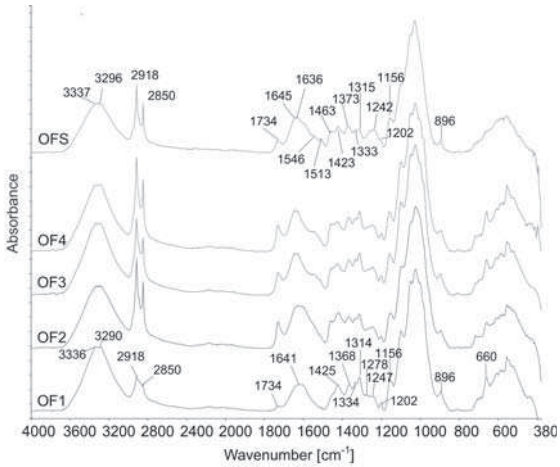


Figure 10: FT-IR spectra of oleaginous flax fibres separated into four length groups (OF1–OF4) and shives (OFS)

the area around 1600 cm^{-1}, corresponding to the aromatic skeleton ring vibration and vibrations owing to adsorbed water, no clear band in the fibre spectra was observed, which suggests that there is still a certain amount of fats and pectins in the fibres. In the shives spectra, an additional band was observed at 1546 cm^{-1}, corresponding to the presence of lignin.

The changes in the magnitude of crystallinity index follow the tendency in the structural changes of cellulose. The crystallinity index of flax cellulose for textile flax fibres was calculated as 0.95–0.80, for oleaginous flax fibres as 0.94–0.73 and for shives of both varieties as 0.72.The index is lower for shives and shorter flax fibres in comparison with that of longer fibres of both varieties. This can be explained by the fact that shives

Table 4: Results of thermogravimetric analysis for all analysed samples: textile flax fibres separated into four length groups (TF1–TF4) and shives (TFS); and oleaginous flax fibres separated into four length groups (OF1–OF4) and shives (OFS)

Sample	T_0 [°C]	T_{max} [°C]	R_{max} [%/min]	Δm_{H2O} [%]	Δm_1 [%]	Δm_2 [%]	m_f [%]
TF1	323	354	12.6	4.3	65.5	9.0	20.5
TF2	324	352	12.8	4.9	64.7	9.1	20.6
TF3	324	352	12.7	5.6	64.4	8.8	20.2
TF4	323	351	12.9	6.2	64.5	7.8	20.4
TFS	309	349	8.9	5.9	64.8	8.4	19.7
OF1	332	367	12.0	5.4	68.6	8.5	16.6
OF2	331	367	12.0	4.6	68.5	8.9	17.1
OF3	321	357	10.2	4.4	67.0	8.6	19.1
OF4	329	363	11.4	4.8	67.9	7.6	19.1
OFS	313	352	8.6	5.2	65.1	8.9	19.8

T_0 – onset degradation temperature, T_{max} – temperature at maximum degradation rate, R_{max} – maximum degradation rate, Δm_{H2O} – evaporation of free water, Δm_1 – weight loss in the second degradation step (degradation of hemicelluloses and cellulose), Δm_2 – weight loss in third degradation step (degradation of non-cellulosic components), m_f – residual weight

and shorter flax fibres contain more amorphous hemicelluloses and pectins. This contributes to the increased absorbance at 2918 cm^{-1}, which is related to the covalent oscillations of CH groups. The deformational oscillations of CH groups at 1368 cm^{-1} depend on the degree of orientation of macromolecules; therefore, the crystallinity index is lower for the shives and shorter fibre samples. A lower content of fat or waxes and pectins leads to the decrease of intensity at 2918 cm^{-1}, and in turn to the increase in the crystallinity index of longer flax fibres. The lower crystallinity index of cellulose and a higher content of amorphous hemicelluloses in shives also influence the higher moisture content in samples, as shown in Figure 6. The lower crystallinity index of shorter flax fibres is probably influenced by a higher amount of pectin and wax in the fibre primary wall (this could be connected with determined lower values of moisture regain, Figure 6) and hemicelluloses in the fibre secondary wall (this could be connected with determined lower values of fibres breaking force, Table 3).

3.5 Thermogravimetric analysis

The thermal stability of flax fibres and shives was determined using the non-isothermal thermogravimetric analysis (TGA). The thermogravimetric analysis results of the tested textile (TF) and oleaginous (OF) flax fibrous material are presented in Table 4, and TGA and differential thermogravimetric (DTG) curves in Figures 11 and 12. Generally, there are three stages of weight loss of the flax fibrous material. The first is moisture evaporation, followed by the decomposition of pectin, hemicelluloses and cellulose, and the third is degradation of lignin. The remaining weight after the third stage represents the percentage of ash.

The thermal decomposition profiles are similar for all analysed textile and oleaginous flax fibre samples. The first weight loss is related to the evaporation of free water in fibre samples. In the stage that begins at 50 °C and ends at around 100 °C, the weight loss of tested fibres varies in the range of 4.3–6.2% for textile flax fibres and for oleaginous flax fibres in the range of 4.4–5.4%. The second weight loss corresponds to the degradation of hemicelluloses and cellulose, and the third is related to the degradation of non-cellulosic components. The second degradation step starts at around 240 °C and ends at around 390 °C. The analysis of flax fibre samples showed no distinct pectin peak at 256 °C [31], although a shoulder can be observed at DTG curves in that temperature region. Similarly, no hemicellulose peak but a small shoulder was detected at 290 °C [31]. There is a cellulose peak that corresponds to the temperature at the maximum degradation rate, which varies in the range from 354 °C for the longest textile flax fibres to the 351 °C for the shortest ones. The temperature at the maximum degradation rate is slightly higher for longer oleaginous flax fibres and amounts to 367 °C, in comparison with shorter OF3 and OF4 at 357 °C and 363 °C, respectively. The changes in the peak temperature along with weight loss and rate of degradation may reveal the variation in the quality of a fibre. The weight changes at the second peak correspond to cellulosic components and show an increase with a high retting degree. The higher peak intensity in fibres is associated with the high crystallinity of cellulose [3]. In this stage, a significant weight loss is observed for both flax fibres; the weight of textile flax fibres reduced by 65.5–64.4% and of oleaginous flax fibres by 68.6–67.0% together with the degradation rate of around 13%/min. The third or lignin peak is significantly smaller in comparison with the primary or cellulose peak. This degradation step for all samples begins at around 395 °C and ends at around 515 °C. However, no distinct peak at 429 °C [31] attributed to lignin could be observed. The weight of textile flax fibres was reduced in this degradation step by 9.1–7.8% due to the degradation of lignin and by 8.9–7.6% in the case of oleaginous flax fibres. At around 700 °C, the tested flax fibrous material possesses a high char residue due to the high cellulose content. This result is consistent with the results reported by other researchers [32]. The residual weight of textile flax fibres amounts to around 20% and of oleaginous flax fibres it varies within the range of 16.6–19.1% (from longer to shorter fibres).

A comparison of thermal stabilities between the fibres of textile and oleaginous flax shows no significant difference. Both samples have a high cellulose content, lower amount of hemicelluloses and pectin, as well as a high degree of fibre quality. This implies that the fibres are thermally stable to up to 240 °C in a nitrogen atmosphere.

Textile and oleaginous flax shives can be considered as thermally stable to up to 220 °C. After 220 °C, a decline in the thermal stability of shives can be observed trough a significant reduction in weight. Lower onset degradation temperatures of shives are

determined compared to flax fibres. The initial weight loss attributed to the evaporation of free water begins at the temperature at around 50 °C with the weight loss of 5.9% for textile and 5.2% for oleaginous flax shives. This is confirmed by a higher moisture release in textile flax shives and a higher amount of free water than in the oleaginous flax shives. The maximum degradation rate occurs at a lower temperature compared to fibres: at 349 °C for textile and 352 °C for oleaginous flax shives. The intensity of the cellulose peak for flax shives is significantly lower compared to the fibres of both varieties, regardless of weight loss of 64.8% for textile and 65.1% for oleaginous flax shives, which are similar to the corresponding flax fibres. The rate of cellulose degradation is lower compared to flax fibres and amounts to around 9%/min. The FT-IR analysis determined a lower crystallinity index of cellulose and confirmed a higher amount of hemicelluloses, pectin and amorphous cellulose in shives in comparison with flax fibres. During the degradation of lignin, the weight of flax shives reduced by about

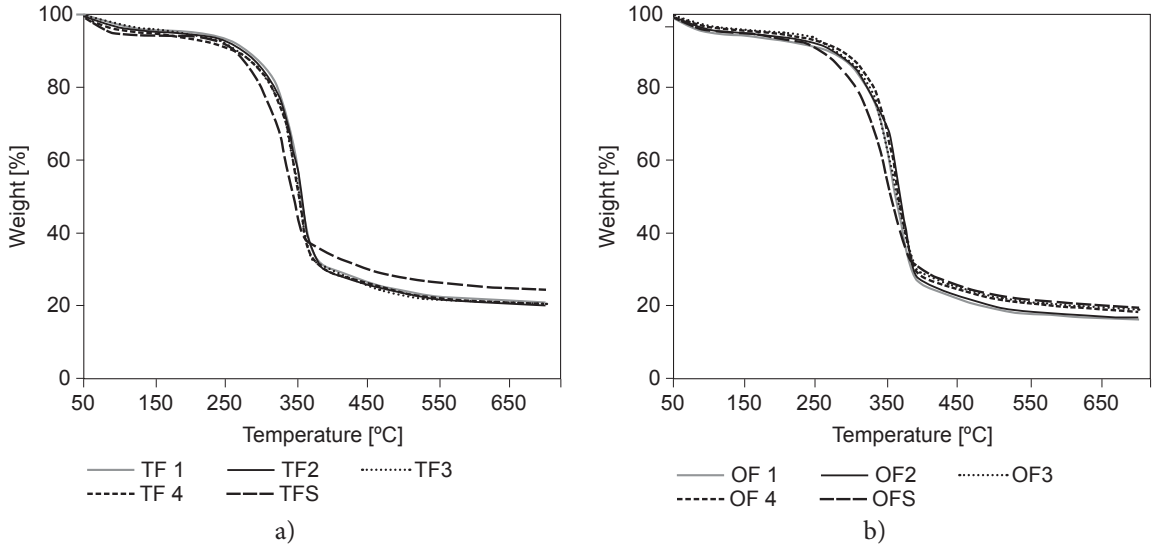


Figure 11: Comparison of TGA curves of: a) textile flax fibres separated into four length groups (TF1-TF4) and shives (TFS); b) oleaginous flax fibres separated into four length groups (OF–OF4) and shives (OFS)

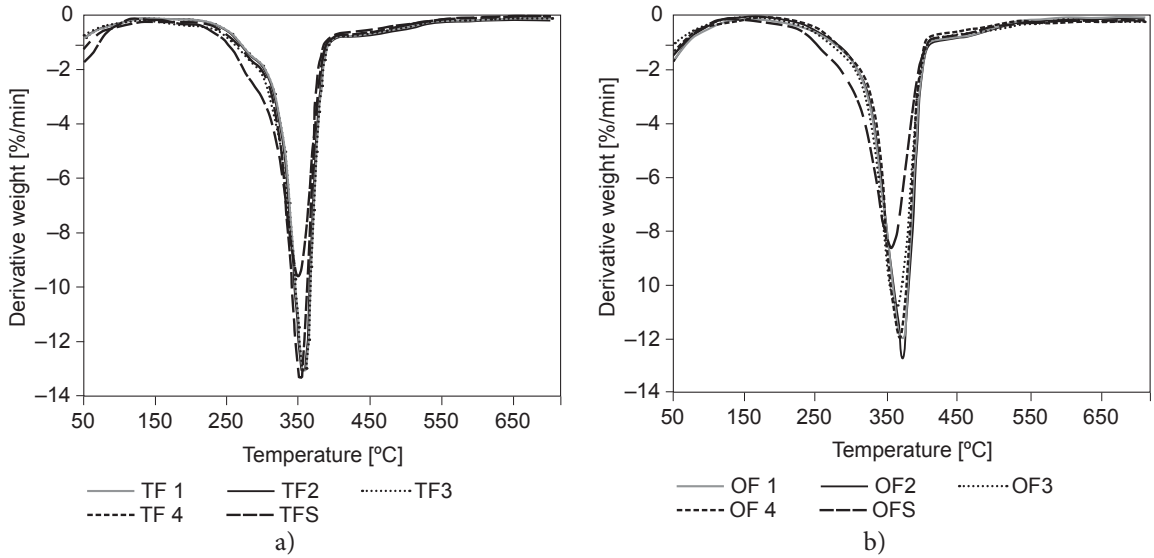


Figure 12: Comparison of DTG curves of: a) textile flax fibres separated into four length groups (TF1-TF4) and shives (TFS); b) oleaginous flax fibres separated into four length groups (OF1–OF4) and shives (OFS)

8–9% and the remaining percentage of ash amounted to around 20%, these values being similar to those of corresponding flax fibres.

4 Conclusion

According to the performed analysis, it was concluded that the measured properties of the textile and oleaginous flax fibrous material were comparable, as well as the properties of individual fibre length groups within the same variety. The optical and SEM micrographs of textile and oleaginous flax fibres for all tested length groups are very similar. The results of the mechanical properties obtained with the oleaginous variety are close to those of the textile variety. The relatively high Young's modulus is determined, which confirms a high flax fibre cellulose content for both varieties. Contrary to the widespread idea, the FT-IR and TGA analysis show no significant difference in the lignin content in flax fibres of textile and oleaginous varieties. The TGA analysis showed for both flax varieties almost the same thermal stability, a high amount of cellulose and a high degree of flax fibre quality. The lower crystallinity index of cellulose and a higher amount of hemicelluloses and pectin were obtained for shives and shorter flax fibres in comparison with the longer fibres of both varieties. The highest values of moisture regain were obtained for shives and the longest fibres of both varieties. The hygroscopic behaviour and presence of pectin and waxes on the surface of flax fibrous material that can lead to the formation of ineffective interface between the fibre and polymer matrix could be modified by different physical and chemical modification processes. Therefore, it was concluded that flax fibres from textile and oleaginous varieties have adequate morphological and mechanical properties, as well as thermal stability for reinforcing polymer composites. As the type of fibre reinforcement (short fibres, roving/yarns, nonwoven or woven fabrics) is very important for the polymer composite resulting properties, it is according to the obtained results possible to select fibres for specific purposes. Shorter fibres can be used for nonwoven mats or unidirectional prepregs; longer fibres can be used for roving yarns and woven reinforcing fabrics – 2D waves, UD waves or multiaxial woven reinforcements. Furthermore, short flax fibres, cut or crushed up to very short length, can be added to the polymer during the manufacturing in extrusion or injection moulding. It should be noted that crushed up flax shives are more appropriate for fillers in plastics, with a lower reinforcing role.

As flax reinforced polymer composites already have a very broad range of application in nearly all sectors of everyday life, this study offers an alternative and eco-friendly fibrous reinforcement material which may have usability potential in Croatia and Slovenia. This point is significant also from the economic perspective, since the whole set of co-product produced by the plants (fibres, seeds, shives) could be valorised. The production of oleaginous fibres could be ensured without using new agricultural lands, thus avoiding the competition with food products. Consequently, farmers could secure several remuneration sources.

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