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Impact of retting and process parameters on the physical and mechanical properties of flax fiber biobased composites

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Abstract

The aim of this research was to evaluate the impact of retting and composite processing on the physico-chemical properties of flax-epoxy biobased composites. Organoleptic analysis showed that the retting time directly reduced the saturation and brightness of flax and biobased composites. The processing temperature also directly influenced the material color. SEM analysis highlighted that the fibers that have undergone the lowest retting remained in technical fiber form due to the presence of a pectin coating. By increasing the retting severity, the technical fibers appeared cleaner and more individualized, thus leading to a higher modulus with increasing retting at the expense of maximum stress and elongation. The intrinsic behavior of flax fibers provided a non-elastic mechanical behavior to biocomposite samples. Stress-strain curves revealed three different areas: at low and high deformation, the behavior was elastic, and at moderate deformation we highlighted a plastic transition. The highest processing temperature provided the best Young modulus for the biobased composites. We also noticed that the Young modulus gradually increased with retting. The effect of retting was even more pronounced by performing a modulus normalization according to the fiber volume. A 40 % improvement in modulus was observed between the lowest and highest retting tested.

Keywords: Flax morphology, retting effect, flax biobased materials, mechanical performances,

1. Introduction

Flax is northern Europe's most cultivated plant fiber. Flax fibers are discontinuous unlike commonly used fibers such as glass or carbon. Their average length is between 2 and 5 cm and tied together in a bundle structure of 13 to 27 unitary fibers, depending on the plant's flax maturity and fiber position. They are bounded together by cortical tissue made of pectin. According to Khennache *et al*, Young's modulus values for flax fiber bundles - i.e., technical fiber - were comprised between 18 and 57 GPa [1]. The broad variability can be easily explained by protocol and material differences. Particular care must be taken during mechanical testing of the technical fiber, by accurately recording the length, cross-section as well as the room moisture content, the flax variety, the treatment applied and the retting conditions. According to the literature, the field-retting and water-retting can both improve Young's modulus and maximum stress but can also reduce the elongation at break. The mechanical improvement can be associated with an increase in cellulose proportion, which is mainly responsible for the plant stiffness. This improvement was also observed in polypropylene-short fibers biobased composites made by injection. For long fibers, most studies use a thermosetting matrix. Flax fibers can be in unidirectional veil or woven together in twill, satin or plain pattern.

Despite extensive testing, for a broader use of flax fibers in industrial sectors, a substantial development and optimization effort is still required. A key problem is the retting step, which is highly dependent on weather conditions. Usually, the retting used for textile application is also applied for the biobased composite application, without knowing if this retting is optimal for this kind of application. Flax must be sufficiently retted to ensure a flawless surface and excellent fiber-matrix interface, without damaging the fiber itself. Special care and treatment are also necessary to avoid structural defects in organic fiber composites. A poorly processed biobased composite can lead to the creation of materials containing defects such as porosity.

This proposed research focuses on physico-chemical and mechanical studies of flax fiber reinforcements and their epoxy biobased composites made by an hot-press processing to improve flax composite material knowledge and industrialization. The retting severity and processing parameters have been examined to better understand their impacts on flax fibers and composite materials properties, regarding morphological and mechanical properties.

2. Materials and Methods

2.1. Material processing

Flax cultivation - Bolshoi variety - has been cultivated at Romilly-la-Puthenay (Normandie, Fra). Flax was seeded on 10/04/2017 and harvested on 13/07/2017. The latter date was calculated as a function of the cumulative degrees received by the plants and fixed at 1014 °C. Winding dates were selected according to a visual estimation of the retting. Consequently, the first winding date was set on 7/08/2017. Flax plants were then scutched to separate the flax fibers from the stem. No hackling steps were applied, nor any chemical, physical and thermal alterations. The used matrix is a XB 3515 epoxy/Aradur 5021 polyamine curing agent. The scutched flax fibers was pre-impregnated by Vitech Composite (Fra). The resulted weight fiber content of the prepregs was given as 50 % ± 3 %. They were then kept at -18°C. Three hot-press processing protocols were proposed. **Table 1** summarizes the used processing variables and the thickness as well as the area density of the resulting samples. Two other biobased composites were prepared with the retted (-) flax and with a processing temperature of 80 and 190°C. They will only be used to analyze the impact of temperature on color transition.

Table 1: Processing protocols

Setup	Retting	Times (min)	T max (°C)	P max (Bars)	Thickness (µm)
1	(-)	370	140	50	495 ± 21
1	(0)	370	140	50	485 ± 22
1	(+)	370	140	50	473 ± 13
2	(-)	175	140	25	553 ± 15
2	(0)	175	140	25	524 ± 18
2	(+)	175	140	25	485 ± 19
3	(-)	130	160	50	506 ± 24
3	(0)	130	160	50	458 ± 13
3	(+)	130	160	50	458 ± 10

(-) under-retted, (0) nominally retted for textile applications, (+) over-retted

2.2. Spectrophotometry analysis

A Konica Minolta CM 2300d spectrophotometer analyzer was used to quantify the color of the flax fibers and biobased composites. The Whiteness Index W^* was calculated with **Eq.1** :

$$W^* = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2} \quad \text{Eq.1}$$

Where L^* represents the coordinate in the L^* axis, a^* represents the coordinate in the a^* axis and b^* represents the coordinate in the b^* axis. Each result was an average of 10 measurements.

2.3. Scanning electronic microscopy (SEM) analysis

Scanning Electronic Microscopy (SEM) analyses were carried out to observe the flax fiber morphology. The tests were conducted at 15 kV with a magnification range from x37 to x200. No coating was applied. Three specimens were analyzed for each material.

2.4. Tensile test for flax fibers

Mechanical tests were conducted using an MTS Criterion 43 tensile testing machine. Thirty-three different technical fibers per retting condition were tested, with working lengths ranging from 14 to 100 mm, and elongation speed fixed at $1 \text{ mm} \cdot \text{min}^{-1}$. This part has been described in detail in a previous study [1]. A new method for calculating the average cross-section of each technical fiber was proposed, using a combination of weight and density.

2.5. Tensile test for biobased composite materials

To investigate the mechanical properties of biobased composites, a Shimadzu tensile testing machine with a 50 kN measuring cell and self-tightening jaws was used. The elongation speed imposed on the sample was fixed at $2 \text{ mm} \cdot \text{min}^{-1}$ and carried out at 23°C and 65 % RH. Dogbone specimens were prepared according to ISO 527. They were cut by laser, with a cutting speed of $35 \text{ mm} \cdot \text{s}^{-1}$. Protective parts were glued to the sample area pinched by the jaws to avoid stresses and premature failure. Five samples were tested for each material.

3. Results and discussion

3.1. Spectrophotometry and morphological analysis of flax fibers

Table 2 shows the variation of the $L^*a^*b^*$ components for flax fibers. Fibers was named (-), (0) and (+), according to the retting severity. A significant decrease of all components was noted. This result was visually reflected by a color transition from yellow to grey, respectively, from the less retted (-) to the more retted (+) flax. Similar observations and trends was also reported by Pallesen *et al.* and Martin *et al.* [2, 3] for flax fibers, and Mazian *et al.* for hemp fibers [4]. Quantitatively, the results were close to those observed by Martin *et al.* [3]. As presented in **Table 2**, the color transition was not linear. The first transition, between the retting (-) to retting (0), reduced the sample saturation without significantly

altering the L* component (P value > 0.05). This can be associated with a possible degradation of soluble components present in flax fibers. Van Soest's results (not presented here) showed that soluble components decreased according to the retting levels. The obtained values were 10.4 %, 6.1 % and 4.5 % which corresponds respectively to the (-), (0) and (+) retting. The measured difference between these results was significant according to ANOVA tests (P-value = 1.58×10^{-4}). The transition between retting (0) and retting (+) was notable by a decrease of the L* component and a slight loss of the b* component and can be attributed by the presence of a microbial biofilm [4], thus promoting the individualization of elementary fibers.

	Retting (-)	Retting (0)	Retting (+)
L* component	57,25 ± 0,89	56,91 ± 1,02	54,10 ± 0,88
a* component	4,01 ± 0,37	2,81 ± 0,23	2,71 ± 0,13
b* component	21,76 ± 0,93	14,92 ± 0,54	12,99 ± 0,55

Table 2: Spectrocolorimetry results for flax fibers at different retting : a) L* component, b) a* component, c) b* component a) Luminance L*a*b* component for flax modalities at different retting

Figure 1 shows the SEM images obtained for the different flax technical fibers examined. Fibers (-) were still present in a tightly bounded technical fiber. The technical fiber cohesion can be provided by soluble compounds (pectins, fats and waxes) still present in the technical fiber [5, 6]. As the severity of retting increased, this coating tended to disappear, leaving the surface of the fibers more visible [3]. These results were also found for the enzymatic retting of flax fibers [7] and date palm fibers [8]. Despite a long retting time, the surface of the elementary fibers did not appear visually degraded.

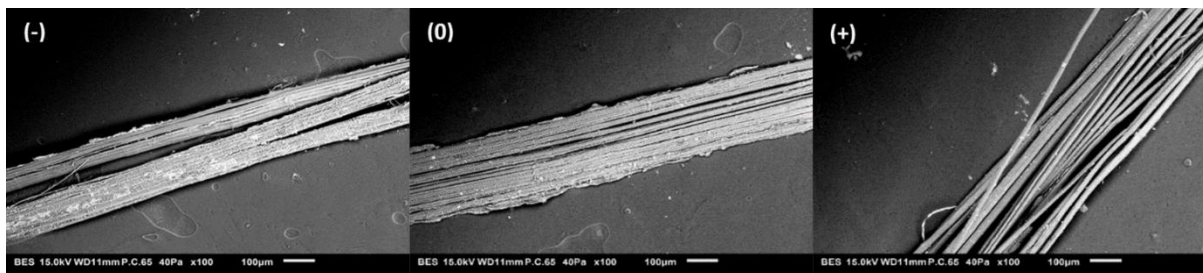


Figure 1: SEM pictures of technical flax fibers a) retting (-), b) retting (0), c) retting (+)

1.1. Tensile analysis of flax fibers

For the tensile analysis of the fibers, two different cases could be considered: i) when the fiber length tends towards 0 mm, then the technical fiber can be assimilated to a huge continuous elementary fiber, with mechanical behaviors similar to an elementary fiber, ii) when the fiber length tends towards 100 mm, then its mechanical behavior can be assimilated to a technical fiber, i.e., a sum of elementary fibers linked by pectic contents. Young's modulus, tensile strength, and failure strain of technical fiber are given in **Figure 2**. When the fiber length reached 0 mm, the retting effect was positive on the fiber rigidity, as Martin *et al.* noted [3], but the retting had a negative influence on the failure properties. This observation can be easily explained by SEM results (**Figure 1**). The retting process dissociated the elementary fibers, resulting in cleaner fiber surfaces [1, 3] and wider fiber spacing [9]. As the stiffness can be associated to the mean stiffness of all the elements, the cross-section decrease due to the

cleaning effect during scutching was positive. However, this phenomenon does not act similarly on the strength because of the criteria of the weakest link. When the fiber length reached 0 mm, all the technical fiber properties decreased when the retting severity increased. A 15 % decrease in Young's modulus and 50 % decrease in the maximum stress was observed. Internal stresses were no longer transmitted by the biological matrix, drastically reducing the strength and rigidity of technical fibers.

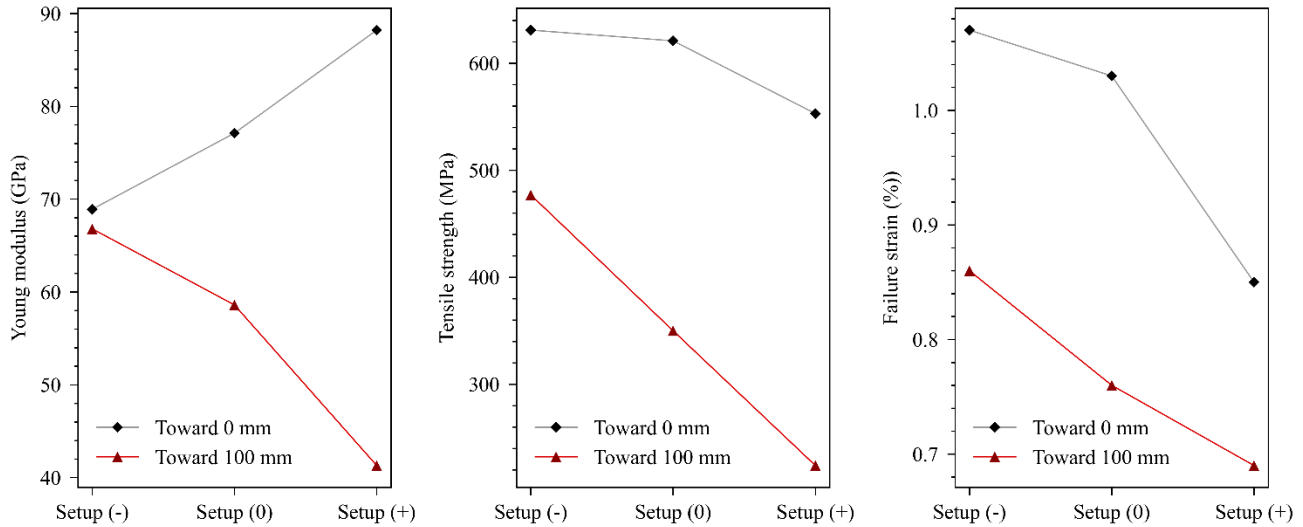


Figure 2: Mechanical properties of technical flax fibers

1.2. Spectrophotometry analysis of biobased composites

Table 3 shows L*a*b* components for biobased composites processed with the setup 1. All the components decreased with the retting severity the resulting material color converged to a darker shade. The same trend was also highlighted for flax fibers. As the retting effect of the flax was still visible on the biobased composite, the epoxy resin did not seem to affect the color transition of the biobased materials, mainly at 140°C.

	Retting (-)	Retting (0)	Retting (+)
L* component	39,72 ± 0,40	39,42 ± 0,30	37,89 ± 0,42
a* component	5,43 ± 0,38	3,36 ± 0,35	3,22 ± 0,48
b* component	14,44 ± 0,62	11,13 ± 0,52	9,89 ± 0,36

Table 3: Spectrocolorimetry results for flax epoxy biobased composites made with setup 1 : a) L* component, b) a* component, c) b* component

Table 4 present the a* component and the Whiteness Index W* according to processing temperature. The a* component increased steadily then remained stable above 160°C, and W* decreased continuously. Visually, these variations translated by a color transition from yellow to orange and finally red to brown. A chemical reaction can be suspected due to a synergy between the process parameters and the flax composite system. Further analysis is in progress to confirm the nature of the chemical reaction.

Processing temperature (°C)	a* component	Whiteness Index W*
80	2,99 ± 0,26	61,36 ± 0,53
140	5,44 ± 0,32	62,23 ± 0,40
160	6,97 ± 0,47	62,58 ± 0,51
190	6,99 ± 0,20	65,07 ± 0,44

Table 4: Effect of processing temperature on a* component and Whiteness Index W*

1.3. Mechanical analysis of biobased composites

Figure 3a) shows the stress-strain curves for the biobased composites. A non-linear stress-strain curve was observed. This non-linear behavior was also confirmed in the literature [11, 12]. **Figure 3b)** shows three areas, with different behavior. Area 1 (0-0.1 % of deformation) was characterized by an elastic behavior. This area was used to calculate the E1 modulus (modulus of small deformations). Area 2 (0.1 - 0.3% deformation) was characterized by a plastic transition. It may be explained by a rapid rearrangement of the amorphous phase of S2 layer, associated with the arrangement of the cellulose microfibrils and thus resulting in a rigidity decrease. Area 3 (over 0.3 % of deformation) was the second elastic transition. The E2 modulus (for large deformations) was calculated between 0.3 and 0.5% of deformation.

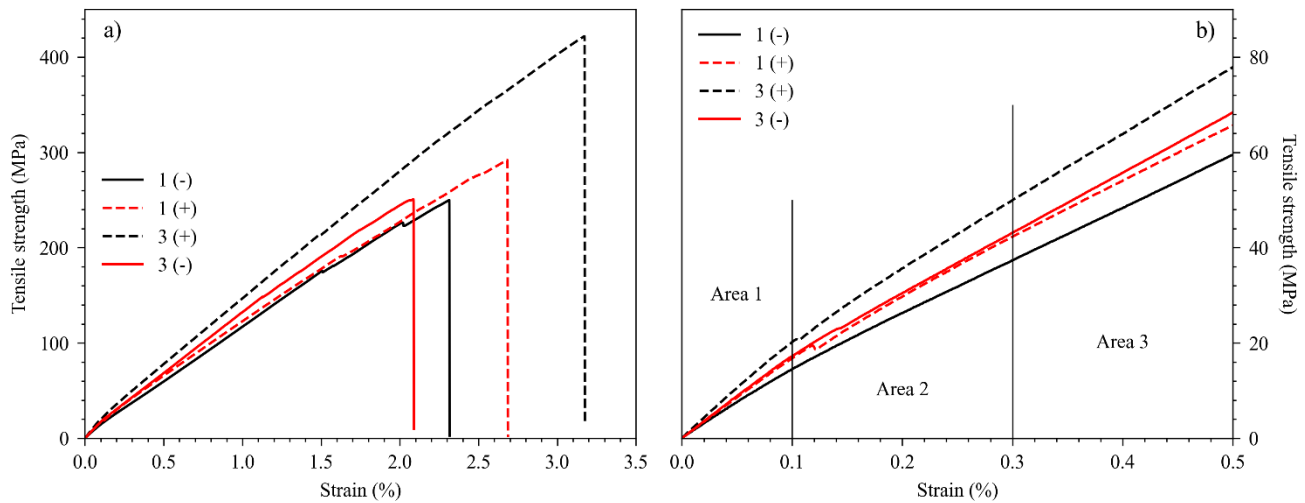


Figure 3: Stress-strain curves of biobased composites a) Global curve, b) Small deformations area

Table 5 shows the E1, E2 modulus, and tensile strength associated with the different biobased composites manufactured. E1 gradually increased with the retting severity. The setup 3 provided the best E1 and E2 modulus. The lowest E1 modulus was found at 14.3 GPa for the composite 2 (-), and the best E1 modulus was found at 19.5 GPa for the composite 3 (+). On the other hand, the E2 modulus ranged from 11.1 to 14.2 GPa. Setup 3 also allowed the best stiffness values, but the setup and retting effect were less apparent. The processing and retting influences on tensile strength were more complex

to analyze than for E1 modulus. The tensile strength increased with the retting for the setup 3, but the retting (0) was better for setups 1 and 2. The lowest and tensile strengths were obtained for the conditions 3 (-) at 251 MPa and 3(+) at 381 MPa respectively.

Setup	Flax	E1 Modulus (GPa)	E2 Modulus (GPa)	Tensile strength (Mpa)
1	(-)	15,42 ± 1,91	12,31 ± 1,02	287,4 ± 25,3
	(0)	16,45 ± 0,98	12,57 ± 0,74	322,2 ± 23,1
	(+)	17,08 ± 0,96	12,37 ± 0,76	279,1 ± 17,9
2	(-)	14,29 ± 0,58	11,11 ± 0,42	283,1 ± 14,5
	(0)	15,09 ± 1,69	11,89 ± 0,28	323,5 ± 33,9
	(+)	16,38 ± 1,46	11,83 ± 1,23	290,2 ± 36,1
3	(-)	16,30 ± 0,83	12,18 ± 0,65	250,9 ± 16,2
	(0)	18,68 ± 0,57	14,20 ± 0,57	350,0 ± 17,4
	(+)	19,48 ± 0,91	13,42 ± 0,59	381,6 ± 32,1

Table 5: Influence of retting and setup on raw mechanical properties a) E1 modulus, b) E2 modulus, c) Tensile strength

To be as rigorous as possible, the mechanical properties of the different biobased composites were standardized according to their fiber volume content. We considered that the mechanical properties of fiber-reinforced composites comply with the rule of mixture given by **Eq.2**:

$$E_c = \eta_0 * \eta_1 * V_f E_f + V_m * E_m$$

Where E_c is the composite young modulus, E_f and E_m are the longitudinal young modulus of the flax fiber and the young modulus of the matrix, respectively. V_f and V_m are respectively the volumic fiber and matrix content. The constants η_0 and η_1 correspond respectively to the orientation efficiency and length efficiency of the fibers. For the purposes of this study, these values have been fixed at 1. **Table 6** shows the evolution of the standardized modulus of elasticity E1. Retting positively impacted the mechanical performance of biobased composite materials. Regardless of the setup used, a 40 % increase in modulus can be observed between retting (-) and (+). The fiber individualization phenomenon can be the responsible for the property's improvement. Although there is no clear effect concerning the processing effect. E1 modulus had no difference from a statistical point of view, although the best result seems to have been achieved for biobased composite 3 (+).

Setup	Flax	Normalized E1 Modulus
1	(-)	0,255 ± 0,032
	(0)	0,313 ± 0,019
	(+)	0,338 ± 0,014
2	(-)	0,231 ± 0,010
	(0)	0,287 ± 0,032

	(+)	0,339 ± 0,030
	(-)	0,244 ± 0,013
3	(0)	0,295 ± 0,009
	(+)	0,349 ± 0,016

Table 6: Influence of retting of normalized E1 modulus

Conclusions

This study studied the physical-mechanical performances of flax-epoxy biobased composites made by thermocompression. From an organoleptic aspect (spectrophotometric analysis), flax showed a two-phase color alteration with increasing retting severity. The a^* and b^* components decreased between the less retted (-) and the more retted (+) flax fibers. This is visually reflected by a color transition from yellow to grey, respectively, for the less retted (-) and the more retted (+) flax.

From a morphological point of view, an individualization of the technical fibers into single fibers due to the retting. This individualization phenomenon was induced by the degradation of the tissue binding the fibers, which was easily degraded by microorganisms. The degradation of the middle lamella was also highlighted by the tensile analysis of the flax fibers. The retting also decreased the $L^*a^*b^*$ components of the biobased composites and the processing temperature affected the visual aspect of the samples.

Regarding the mechanical behavior, the influence of retting on the mechanical properties of technical fibers at 0 mm was disparate. Retting improved the modulus but decreased the maximum stress and elongation at break. This was directly linked to the cleaning of the fibers. The influence of retting on the mechanical properties of technical fibers at 100 mm was negative for all the mechanical properties tested, due to the loss of the cohesive system. The mechanical analysis of the biobased composites revealed three different behaviors. Two elastic behavior were visible, separated by a plastic transition. It also appeared that setup 3 provided the best modulus compared to the other setups. Also, the modulus seemed to be directly linked to the retting applied. The processing parameters didn't significantly affect the mechanical properties of biobased composites.

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