FLAX FIBRE REINFORCEMENT CHARACTERIZATION FOR UNIDIRECTIONAL COMPOSITE APPLICATION

Gaffiot Lauric[1], Heux Laurent[1]

[1]CEntre de Recherche sur les MAcromolécules Végétales, Centre National de la Recherche
Scientifique, 601 Rue de la Chimie, 38400 Gières, France
Email: lauric.gaffiot@cermav.cnrs.fr, Web Page: https://www.cermav.cnrs.fr/fr/user/2327
Email: laurent.heux@cermav.cnrs.fr, Web Page: https://www.cermav.cnrs.fr/user/1403

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Abstract

Natural fibres are hydrophilic cellulosic material that requires chemical modification to enhance its affinity with hydrophobic polymer matrices, in order to reach the performance needed for structural applications. In this study, an aqueous treatments has been designed for the compatibilization of the technical flax fibres. Micromechanical test shows a noticeable positive effect on the fibre-matrix adhesion, and a slight increase in the technical fibre mechanical properties, which are essentially governed by the probability of the presence of defaults (kinks, knees…) and by the elementary fibre length. At a higher scale, technical fibre rovings breaking mechanism lies on fibre breakage, disentanglement and sliding of technical fibres, resulting in lower mechanical properties. The formation of such rovings induced by agglomeration of fibers during the treatment explains the low strength of the composite. Finally, an important disorientation of the unidirectional ply that increased with the treatment process might partly explain the difference between the simple calculated mixing law predictions and observed properties.

1. Introduction

Natural fibres offer a sustainable alternative to synthetic fibres for composite applications in many domains. The flax fibre is one of the strongest natural fibre, and its historic use in textile industry in Western Europe made it cultivable and accessible for composite elaboration [1]. On the contrary of synthetic fibres, flax is not continuous and is itself a composite: the elementary fibres, which are single plant cells, are organized in bundles to form technical fibres with interphase of pectins and hemicelluloses. The oriented crystalline structure of the cellulose microfibrils in the elementary fibres makes them strong and stiff in tension, whereas the technical fibres are less resistant because of the weaker polysaccharide interphase [2]. In addition, flax is a hydrophilic cellulosic material that have a poor interfacial bonding with hydrophobic matrices. Chemical treatments have been developed to improve the fibre-matrix adhesion to reach the performances needed for structural applications [3].

In order to assess the effects of such treatments, the characterization of technical fibres interface with the matrix thanks to micromechanical test may show adhesion improvement, as tensile test may give information on the fibre strength itself. The mechanical properties of the technical fibre are governed by its structure: the breaks is worth to be localized at the pectic interface between elementary fibre[4]. At a higher scale, technical fibres bundles (or even rovings of technical fibers) breaking mechanism would be dominated by fibre disentanglement, sliding and technical fibre

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breakage. This evolution in the rupture process, from the elementary fibre to the roving, and by extension to the flax unidirectional ply, explains the decreasing of the mechanical properties when increasing the scale of observation. In this study, a compatibilization treatment is characterized on technical fibres, and structural composite issue are linked to its formulation. The fibre scale effect is investigated to explain the resulting composite properties.

2. Experimental

2.1. Materials

Flax fibres, and flax unidirectional sewed plies have been provided by Chomarat. The flax reinforcements are 720 g/m² unidirectional (UD) plies with a 30 g/m² glass fibre weft and polyester veil and stitching yarn.

2.2. Composite elaboration

Two 20 g Flax plies are manually impregnated with 50 g of epoxy resin, and a 2 plies composite is pressed at 115° and 20 bars for 10 min. The obtained composite have a 56 % volumetric fibre fraction, measured by nuclear magnetic resonance (NMR) spectroscopy.

2.3. Tensile test

The tensile test are realized on a Shimadzu AGS-X. The technical flax fibres have been glued on a paper frame, and are tested with a 20 N cell as rovings require a 500 N cell, and both are tested at a 1 mm/min strain rate with a clamping length of 3 cm. The section has been investigated by the linear mass, measured for each fibre and roving, and density (1.48 g.cm$^{-3)}$ ratio. The composite samples have been cut in a rectangular shape of 2 X 20 cm with a Mafell MT55 cc circular saw equipped with a trapezoidal tooth blade. A 10 cm clamp length has been used during the test with a measurement of the strain on 5 cm thanks to a Shimadzu TRS view X Extensometer. The strain rate is 2 mm/min for the composite.

2.4. Fragmentation Test

Technical flax fibres are fixed in tension 1 mm up to the bottom of a Teflon mold. Degazed epoxy is poured in the mold and the polymerization is done at 115° C for 10 min. Fragmentation samples of 30 x 4 x 2 mm are cut thanks to a diamond blade saw. The fragmentation is realized at 60° on a Minimat tensile machine at 0.05 mm/min to reach a 10% deformation on the 2 cm clamp length. According to the specific behavior of the technical fibres during this test, the results will be exploited here only in a qualitative way, as a comparison of the different fibre treatments.

2.5. Microscopy

Scanning electron microscopy has been realized thanks to a Quanta 250 Feg microscope from FEI. The transversal cuts have been realized on Optic epoxy resin inclusion of composite samples, thanks to a Leco VC 50 diamond saw. The longitudinal cut have been realized on composite slices, and observed in optic microscopy with a Zeiss axioplan 2 equipped with axiophot 2 camera.

3. Results and discussion

3.1. Technical fibres properties

The technical flax fibres are bundles of elementary fibres which are themselves made of rounded shape cell walls. The elementary fibre mechanical properties are comparable to those of the

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glass fibre, whereas the technical fibres have lower properties due to the weakness of the fibre-fibre interface in the bundles [5]. However, the elementary fibres are between 1 and 5 cm long and are too short to be organized in unidirectional reinforcement, as the technical fibres are more than 10 cm long. So we decided here to assess the influence of chemical treatments on the technical fibres, with a clamping length close to the elementary fibres one.

The tensile test are realized on 10 samples for untreated and treated fibres. Both average stress at break and Young modulus increase slightly, respectively from 808 to 1015 MPa and from 58.7 to 64.2 GPa thanks to the treatment (Fig.1).

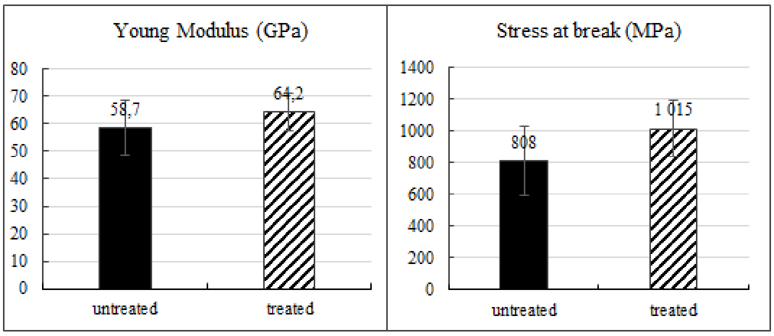

Figure 1. Stress at break and Young's modulus of treated and untreated fibres. Standard deviations are indicated by the error bars.

The fibre matrix adhesion is a key point in composite materials design, and specific chemical functions have to be grafted onto the fibre surface in order to create covalent bonds between cellulose and epoxy resin. Moreover, the fibre surface modification might have a positive influence on the impregnation, because of hydrophilicity change. A micromechanical single fibre fragmentation test is done on treated and untreated flax technical fibres to assess the quality of this interface. The single fibre fragmentation test allow the measurement of interfacial shear stress, and has been used on flax fibre to characterized fibre-matrix adhesion [6]. This method have been applied on technical fibres in order to understand fibres behavior in composites and as a comparative analysis to assess adhesion improvement.

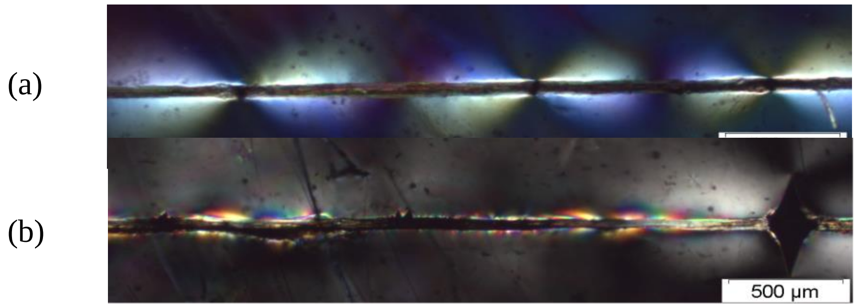

Figure 2. Microscopic observation of untreated (a) and treated (b) technical flax fibres fragmentation samples on polarized light

The untreated fibre presents a classical behavior with periodic fibre breaks in the center of butterfly shaped deformations zone of the matrix that appear birefringent with shiny white and blue colors between cross-polars (Fig.2a). The treated fibre shows a very specific behavior. First, only a few breaks are visible along the 2 cm sample, and they are accompanied by important damages on the matrix. Matrix cracks, as seen at the right handside of Figure 2b, start from both fibre ends. These phenomena are known to occur with strong bonding between fibre and matrix. On the other parts of the sample, the fibre became black, and a thin and quasi-continuous birefringence zone appears at the

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interface. This birefringence is most probably due to interfacial shear and frictional stresses and strains. Zoom on these specific areas reveal many cracks in the matrix all along the interface.

This behavior prevent the quantitative measurements, and is not fully explained for the moment. A degradation of the technical fibre most probably occurs due to the important shear stress, causing a loss of cohesion between the elementary fibres in the technical fibre, not encountered in for glass fibres, which are much more regular. In conclusion, we can even observe an unusual behavior like matrix cracks and deformations which are the sign of an adhesion improvement [7]. Technical fibres characterization shows the pertinence of our treatment, with a better adhesion and a positive influence on their tensile strength.

3.2. Technical fibre roving properties

Technical fibres rovings have been extracted from the reinforcement plies, containing around 200 fibres. The mechanism of rupture involved technical fibre breakages, disentanglements and sliding, and result in low mechanical properties both in maximum stress and young's modulus, with respectively 250 MPa and 13.5 GPa as shown on fig. 3. While interface resistance between elementary fibres is ensured by pectic cement in technical fibres, only friction mechanism are implied in the case of the rovings. It is interesting to note that the standard deviation are low in this case, explained by the homogenization of the breakage process and the normalization of the technical fibres defaults.

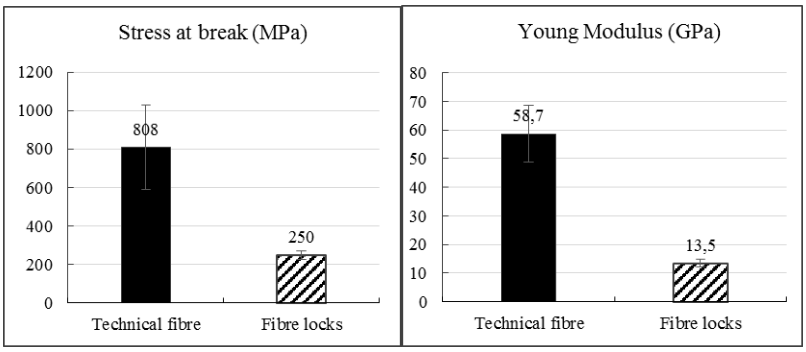

Figure 3 : Stress at break and Young's modulus of treated and untreated fibres and rovings. Standard deviations are indicated by the error bars.

This behavior is a good illustration of the scale effect specific to the flax fibre and its structure. The elementary fibres develop very good mechanical properties as its breakage depends on its intrinsic strength, affected by defaults presence. Then, the technical fibre strength lies on pectic interface and elementary fibre breakage, resulting in a drop in the mechanical properties. At a superior scale, the roving (as in the reinforcement ply) will break without interface cohesion, inducing even lower strength.

3.3. Composite properties

The final investigation on the treatment is done thanks to the composite study. The mechanical characterization should be influenced by compatibilisation effect, taking into account the process efficiency to treat the UD plies. However, the tensile test shows a drop from 19.7 to 10.9 GPa for the Young's modulus and from 271 to 167 MPa in ultimate stress between untreated and treated flax composites.

Such differences in the properties of treated and untreated flax composite wasn't expected considering the previous results on fibres. No major modification of their strength have been measured, and in view of these results, another key issue have to be identified. The fibre-matrix ratio measurement of the samples have been controlled by Solid State NMR and reach 56% for both treated

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and untreated flax composite. A further analysis of the composite structure have been done by optic and scanning electron microscopy (MEB) on transversal and longitudinal sections.

The observation of transversal sections of the composite allows the characterization of the technical fibre dispersion, and the penetration of the matrix into the technical fibre bundle, to the elementary fibres. The MEB observation of the treated flax composite (fig. 4, left) reveals numerous fibre-fibre contacts reproducing rovings inside the matrix as circled in green, and a bad penetration of the resin into the technical fibres. The fibre-fibre interface being weak, thus it will not allow a good stress transfer from the matrix to the fibre, and hence breaking mechanisms similar to the flax rovings [8]. In these case, despite an improvement of the adhesion between the fibre and the matrix, the resulting properties of the composite will drop. In fact, the roving formation inside the composite allows a simple comparison by applying technical fibres and rovings properties in a simple rule of mixture taking into account the mechanical properties of the individual components and their respective volume fraction as shown in table 1. It clearly points the link between roving properties and treated composite results.

Table 1. Comparison of measured composite properties and rule of mixture predictions applied on technical fibres and rovings for 56% fibre ratio in epoxy.

	Technical fibre rule of Mixture Prediction	Untreated composite	Rovings rule of Mixture Prediction	Treated composite
E (GPa)	36	19	9	11
σ (MPa)	495	271	174	167

This phenomenon has been induced by a bad formulation of the treatment, which have coated the fibres and stuck them together. In comparison, the untreated flax composite observation shows well dispersed technical fibre, with a quiet good impregnation. Only few elementary fibre bundles remains, as circled in white (fig.4).

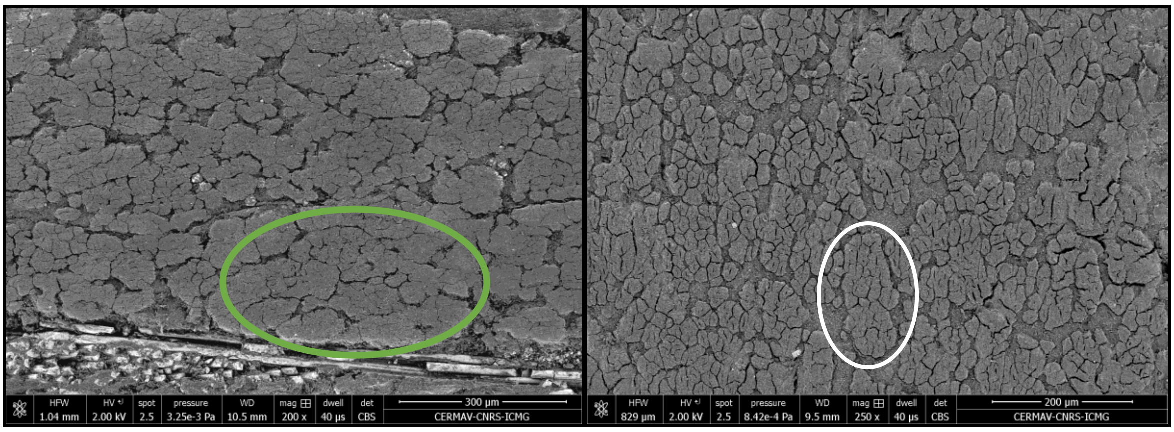

Figure 4. Transversal MEB observation of a flax treated (left) and untreated (right) composites. Circled in green a typical technical fibre roving, and circled in white a technical fibre bundle of elementary fibres.

The agglomeration of fibers couldexplain the difference between treated and untreated flax composite properties, but is not sufficient to interpret the difference between the mechanical properties of the untreated composite and the rule of mixture prediction, even with a poor adhesion.

However, the rule of mixture suppose a perfect UD structure. One of the possible deviation beween the predicted and measured properties can arise from the disorientation of the fibres within the composite. To complete the structural study, longitudinal sections of flax composite and glass fibres are realized and observed in optic microscopy (fig.5). It reveals important flax fibres deviation from the unidirectional axis that reach more than 20°, and particularly at the stitching point of the

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reinforcement. The solicitation of the fibre during mechanical experiment depends on its orientation, with a tensile stress for a good orientation (from 0 to 5°), whereas such deviation will induced also a shear solicitation. This will lead to a drop of the composite mechanical properties because of an increased stress at the fibres interfaces and particularly in case of a bad impregnation, where the fibre-fibre interface low shear resistance will enhance the phenomenon[9].

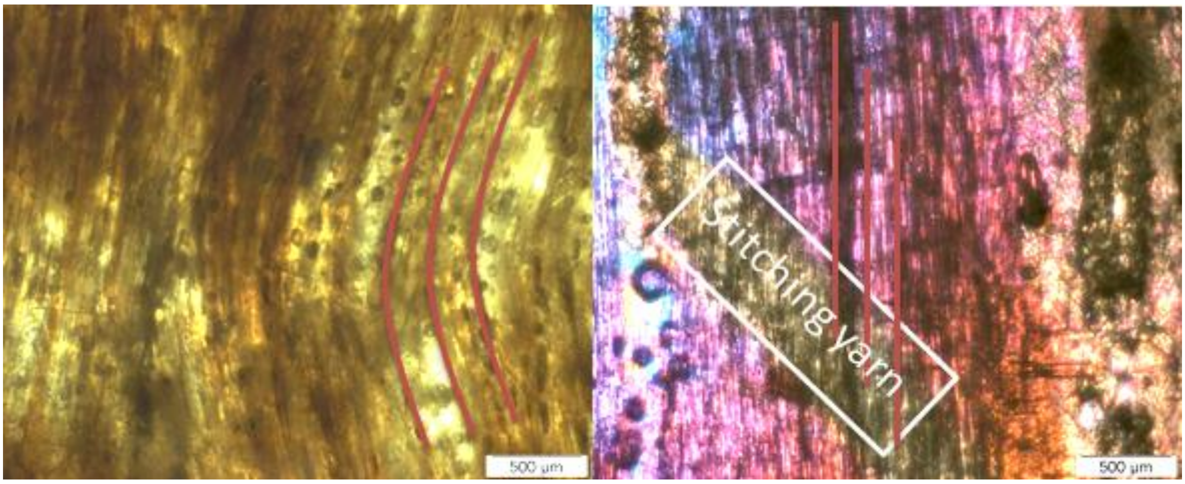

Figure 5. Longitudinal observation of flax (left) and glass fibre (right) composite in optic microscopy. The main orientation are indicated by red lines, as the stitching yarn are marked in white.

The fibre deviations are observed on both treated and untreated flax reinforcement andare amplified at the stitching points, where the polyester yarn compress the flax rovings. Besides, the microscopic observations reveal that the phenomenon is more important and more frequent on the treated reinforcement. It can be explained by the treatment process, where the wet plies goes through several tough winding and unwinding steps. As fibres are more mobile when the ply is wet, some buckles defaults appears, which might induce fibre deviations after composite elaboration.

The composite study shows the influence of the treatment on impregnation, but furthermore the prevalence of the composite structure on its properties.

4. Conclusion

A treatment has been established to increase the flax fibres adhesion with the matrix. Tensile test and micromechanical experiment have been led on technical fibres in order to assess its efficiency. The fragmentation test shows a better adhesion after treatment, and a slight increase in the fibres tensile properties. At a higher scale, rovings (or bundles) of technical fibres have also been tested. Their breaking mechanism has been shown to mainly depend on the fiber-fiber interface andis coherent with the observed svere in terms of mechanical properties. Then, the flax UD composites have been studied revealing reduced mechanical properties after the compatibilization treatment. Instead of promoting the technical fibres impregnation, this formulation has stuck the fibres together, forming rovings inside the composite. The low fibre-fibre interface strength appears as a weak point, avoiding a good stress transfer from matrix to neither technical nor elementary fibres. Besides, a longitudinal study of the UD composite reveals important fibre deviations, amplified by the treatment process.

The characterization of new treatments for flax fibres composite applications have to be considered at different scales that might be considered witha top-down approach. As the composite structure has a major influence on its properties, it has to be optimized to measure any improvement due to the treatment. Once the best ply structure and treatment process is determined, the study of the

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fibre on tensile and micromechanical test allows the elaboration of pertinent treatments that can be then validated on fully optimized composites.

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