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Multi-scale study of the adhesion between flax fibers and biobased thermoset matrices

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ABSTRACT

The environmental impact of composite materials made with a thermoset matrix can be reduced in two ways. First, glass fibers can be replaced by natural fibers. Second, petrochemical components from the matrix can be replaced by biobased renewable equivalents. The quality of the interface between the matrix and the fibers has a strong influence on the composite mechanical properties. In this study, tensile performances of flax fibers and commercially partly biobased epoxy and polyester matrices have been investigated and corresponding unidirectional composites were elaborated. Their mechanical performances are in accordance with fiber and matrices properties, taking into account fiber dispersion. Then, at the microscopic scale, the debonding test was used; a great adhesion between flax fiber and thermoset matrices was highlighted. Finally, tensile tests on ±45° laminates were carried out to create an in-plane shear at the macroscopic scale. Interestingly, the results obtained at the macroscopic scale are well correlated to the ones given by the debonding test at the microscopic scale.

1. Introduction

In order to develop high performance composite materials at a moderate cost, the choice of the matrix is oriented toward a thermoset matrix. The environmental impact of composite materials made with a thermoset matrix can be reduced in two ways. First, glass fibers can be replaced by natural fibers. A recent study showed that natural textiles materials are now suitable for engineering applications [1]. Amongst the natural fibers, flax fibers, in particular, have been investigated and have been shown to be competitive, owing to their good mechanical properties [2–4], low density, and wide availability in France [5]. In the stem, fibers are gathered into bundles and have a polygonal section. Fibers are linked to one another by a middle lamella constituted of pectins, hemicelluloses, lignins, and wax. Flax fibers are made up of two (primary and secondary) concentric cell walls with a void in the middle (lumen), and the secondary wall itself is divided into three layers. The external primary wall is mainly constituted of pectins [6] with some poor crystallized cellulose [7]. The thickest layer within the secondary wall (S2) consists of cellulose microfibrils which are well organized and oriented according to an angle called the microfibrillar angle (MFA). This layer plays an important role in the mechanical behavior of the fiber. The cellulose in flax cell wall is embedded in an amorphous matrix composed of hemicelluloses and pectins. Additionally, all the components which may be found in the fiber composition contain hydroxyl groups. They will play an important role in the linkage with the matrix.

Beside the reinforcement, the second way to improve the environmental impact of thermoset composites is to replace petrochemical components from the matrix with biobased renewable equivalents. Amongst the thermoset resins, epoxy and polyester resins are the most commonly used for high-performance composites and their association with flax fibers allows to obtain efficient composites [8–10]. The main drawbacks for the use of thermoset resins are their difficult recyclability and the toxicity of their constituents. The polyester resin, usually a solvent, is the styrene, which is a hazardous air pollutant and volatile organic compound. During the epoxy resin common synthesis, an epoxy precursor reacts with an amine or acid anhydride hardener. In order to reduce the environmental impact of the thermoset resins made with petroleum reserves, alternative renewable resources are available. The renewable substitutes may be either the epoxy precursors or the hardeners. Epoxidized oils can be good candidates as

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epoxy precursors. Since 1996, natural triglyceride oils have been used as a basis for polymers, adhesives, and composite materials [11,12]. On the one hand, the epoxidized triglyceride oil can react with an amine or anhydride hardener to produce an epoxy matrix resin. On the other hand, in the polyester field, the triglyceride oil can be transformed into fatty acid monomers, which are alternatives to styrene because of their low cost and low volatility [13]. Biobased thermoset resins are often mentioned as poor mechanical property resins. Indeed, because of the low reactivity of epoxy groups and the tendency for intramolecular bonding, any epoxidized oil leads to poorly cross-linked materials with limited thermal and mechanical properties [14–16].

Once the matrix and the reinforcement have been selected, the adhesion between these two components is crucial to determine the composite performance. Indeed, a strong adhesion at the interface is needed for an effective transfer of stress and load distribution throughout the interface. In a thermoplastic matrix, the link between fiber and matrix is ensured by physical interactions whereas in a thermoset matrix, the adhesion results from chemical bonding between both components [17,18]. The microbond test [19] is commonly used to determine the strength of the interfacial bonding. The interfacial shear strength (IFSS) has been evaluated via this test by different authors for flax fibers/petrochemical epoxy systems [20–22] and flax fibers/petrochemical polyester systems [10].

Several macroscopic mechanical tests [23] are sensitive to the interfacial properties. These tests include transverse tensile, in-plane ±45 tension, Iosipescu, and short beam shear tests. Concerning biocomposites, only a few studies have used these tests. Meredith et al. [24] used the short beam test on flax/epoxy pre-pregs. They found interlaminar shear strength (ILSS) between 10.7 and 23.3 MPa depending on the flax fabrics. Yongli et al. [25] prepared flax/glass fiber reinforced hybrid composites with a phenolic matrix, with varying fractions of flax and glass. They measured the ILSS by the short beam strength test for their different hybrid composites. The lowest ILSS (19.35 MPa) was found for the glass fiber reinforced composite; the flax fiber composite exhibited an ILSS of 24.45 MPa, and the hybrid glass/flax fiber composite obtained the highest ILSS at 31.12 MPa, owing to bridging between glass fibers and flax fibers. There are even fewer data regarding the shear properties measured by the in-plane shear test on ±45 laminates. Baley [26] used the in-plane shear test on ±45 flax/polyester and glass/polyester laminates. Le Duigou et al. [27] used the same test for flax/PLLA laminates to evaluate the influence of the thermal history during the fabrication process.

The purpose of this article is to establish whether partially biobased epoxy and polyester resins can compete with their petrochemical equivalent in flax-reinforced biocomposites. The mechanical properties of the reinforcement and biobased thermoset resins have been investigated by tensile testing. Unidirectional composites are manufactured by compression molding with several biobased matrices. Their properties are evaluated under tension. In addition, a multi-scale analysis of the adhesion between matrices and flax fibers is considered. At the micro scale, the IFSS is determined via the debonding test, and results are correlated to the ILSS obtained via the in-plane shear test on ±45 laminates.

2. Experimental details

2.1. Flax fibers

The flax fibers, harvested in 2009 and belonging to the Melina variety, were supplied by the La Calira company (Picardie, France). Fibers were dew-retted to help fiber extraction and then scutched by the flax producer. No further treatment was applied to the fibers. They were manually extracted for tensile and debonding tests. Under the form of unidirectional tapes of untwisted yarns, they were sewn together with cotton thread (Fig. 1). Their basic weight was around 250 g/m^2. They were also used for making the composite samples for the in-plane shear test (Fig. 1).

2.2. Tensile testing on single fibers

Single fibers were manually extracted and glued on cardboard supports with an elliptical window. Tensile tests on single flax fibers were carried out at a controlled temperature (23 °C) and relative humidity (48%), and longitudinal mechanical properties (Young's modulus, ultimate strength and failure strain) were determined. Due to the short fiber length (about 20–30 mm), a gauge length of 10 mm was chosen. The fiber was clamped on a universal MTS type tensile testing machine equipped with a 2 N capacity load cell and loaded at a constant crosshead displacement rate of 1 mm/min up to rupture. The determination of the mechanical properties was made in accordance with the XP T 25-501-2 standard [28] which takes into account the compliance of the loading frame. The mechanical properties result from 71 fibers. Before the tensile test, the diameter of every fiber was measured with an optical microscope. The diameter is the mean of three measurements at different locations on the fiber.

2.3. Epoxy and polyester matrices

The study focused on six commercialized epoxy and polyester matrices. Given that each main resin producer has its green range of matrix, only matrices with renewable carbon content higher than 50% were retained as "partially biobased matrix". A petrochemical reference was also selected. Table 1 shows the matrices under study and their characteristics (bio-content, origin of bio-content and curing specifications). The bio-content is not always measured according to the same method. The U.S. standard ASTM: D6866-12, based on the carbon dating method, enables the determination of the renewable carbon content. The bio-content can also be calculated by the mass ratio between renewable components and the total matrix weight.

2.4. Samples preparation

2.4.1. Matrix plates

For each matrix, a plate was cast between two steel sheets separated by a silicon join in order to obtain a 3–4 mm thick matrix plate.

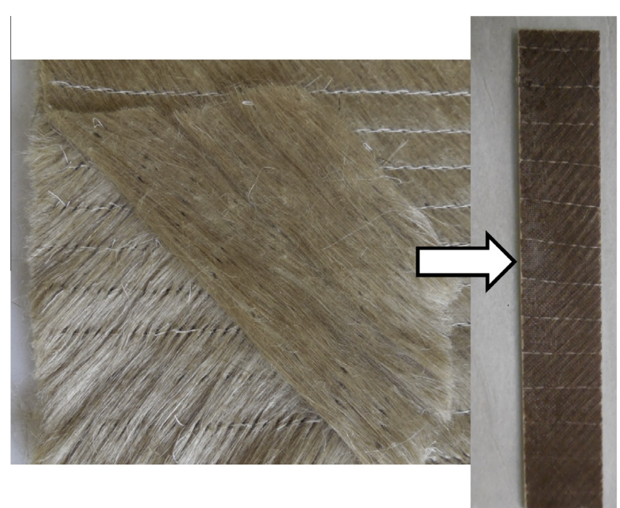

Fig. 1. Sewn unidirectional flax tapes used to manufacture composite samples for the in-plane shear test.