ASSESSMENT OF INTERFACIAL ADHESION OF FLAX YARNS IN THERMOSET MATRICES: EFFECT OF DIFFERENT SURFACE MODIFICATION TREATMENTS

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Abstract
Despite the interest in using natural fibres as reinforcements in polymer composites to replace glass fibres, the use of composites based on natural fibres in semi- or structural applications is still limited. This is mainly due to the weak adhesion property between the natural fibres and the polymeric matrix. The present experimental work is focused on the assessment of the effect of different physical and chemical treatments able to increase the adhesion of flax fibres with hydrophobic polymer matrices but with a limited use of chemicals, in an attempt to preserve the environmentally friendly character of plant fibres. In particular a plasma polymerization treatment and enzymatic treatments have been performed on flax yarns. Single-fibre fragmentation test (SFFT) has been performed to investigate the degree of adhesion between the untreated and treated flax yarns and resins (epoxy and vinylester). Depending on the quality of the adhesion, more or fewer fragments were observed and an estimate of the interfacial shear strength (IFSS) has been obtained. Micro-CT analysis has also been used to assess interfacial properties of the single yarn composites and to perform a reconstruction of the breaking area of the flax yarn.

1. Introduction

In recent years, natural fibres are increasingly being used as reinforcements in composite materials [1-2]. This growing interest from scientists and society is essentially due to the continuous research of a more sustainable development and to the aim to limit the impact of materials on environment. Among the different natural fibres, particularly interesting is the flax fibre, characterized by good mechanical properties, low density and wide availability [3]. Despite these benefits, flax fibres are characterized by several drawbacks such as high moisture absorption, low temperature limitations, poor microbial resistance, inferior fire resistance, poor fibre/matrix adhesion, low transverse and compressive strength, poor dimensional stability, local and seasonal quality variations [4]. Among these disadvantages, the poor fiber/matrix interface bonding properties play a key role in the industrial utilization of flax fibres. The adhesion between matrix and its reinforcement is crucial to determine the composite performance. A strong adhesion at the interface is needed for an effective stress transfer and load distribution throughout the fibre/matrix interface, thus ensuring the composites good mechanical properties. In this context, the chemical composition of flax fibre plays an important role on the interfacial properties of a composite. Cellulose, hemicellulose, wax, lignin and pectin represent the main constituents of flax fibre [5]. The components that principally contribute to the physical properties of flax fibres are cellulose,

hemicellulose and lignin. In particular, cellulose is the stiffest and the strongest organic constituent in the fibre. However, cellulose is a semicrystalline polysaccharide with a large amount of hydroxyl groups (-OH), giving a hydrophilic nature to flax fibre when used to reinforce hydrophobic matrices. The bad compatibility between the typically hydrophilic reinforcing flax fibre and the more hydrophobic polymer matrices is the leading cause of the weak fibre/matrix interface of natural fibre reinforced composites. To better integrate natural fibre reinforced composites on an industrial scale it is important to enhance their mechanical performance improving the interfacial adhesion properties between flax fibres and polymer matrices. In literature different works have investigated the adhesion quality between cellulose fibres and polymer matrices [6]. Single fibre fragmentation test (SFFT) represents one of the most widely used test for interfacial shear strength (IFSS) assessment in both synthetic [7] and natural fibre composites [8]. In this type of test, a long fibre is completely embedded in the polymer matrix and the sample is loaded axially in the fibre direction with a tensile test. During the loading, because of the smaller ultimate strain of the fibre compared to the matrix, the fibre starts to fragment when the fibre ultimate strain is exceeded. Depending on the adhesion quality, more or fewer fragments are formed. This fragmentation process continues until the transferred shear stresses are too small to involve other fragmentation of the fibre. From the lengths of these fragments the interfacial shear strength value can be calculated. The purpose of this article is to investigate the possibility to use fragmentation test to assess the adhesion of flax yarn with different thermoset resins. In particular epoxy and vinylester matrices have been selected. It is important to underline that, in this study the fragmentation testing was transferred to the scale of single yarn specimens. A specific metallic mold has been designed to manufacture monofilament composite samples, where the filament is represented by a single flax yarn embedded in the polymer resin. The adhesion quality between flax yarn and both epoxy and vinylester matrices has been assessed in term of critical fragment length, debonding length and interfacial shear strength. High-resolution microtomography (1.5 µm) allowed to perform a volumetric reconstruction of the breaking area of the flax yarn. With a view to optimizing the fibre/matrix interface quality, a plasma polymerization treatment and an enzymatic treatment have been performed on flax yarns, and fragmentation tests have also been realised on samples made with treated yarns.

2. Materials and methods

2.1. Materials

Individual flax yarns have been extracted by hand from Biotex fabric (*Linum usitatissimum*) supplied by Composites Evolution (UK). It is a 2×2 twill fabric (200 g/m^2), commercialized without any specific sizing agent. Concerning the polymer resins used for the study, thermoset epoxy and vinylester resins have been selected. In particular, Prime 27 epoxy infusion resin, delivered by GURIT, and Advalite VH-1207 vinylester infusion resin, supplied by Reichhold, were used.

2.2 Single yarn fragmentation tests

The fragmentation testing was performed with an Instron E1000 ElectroPuls test machine with a load cell of 2 kN and using a crosshead speed of 0.005 mm/min. Tests have been performed on single flax yarn composites manufactured by using a specific metallic mold. Before casting, flax yarns were conditioned at 45 °C for 24 h for moisture elimination. For each specimen, the average flax yarn diameter was evaluated by optical microscopy before each fragmentation test. According to Ohsawa et al. [9], the critical yarn length has been evaluated using equation (Eq. 1):

$$l_c = \frac{4}{3} \cdot l_{av} \quad (1)$$

where l_{av} is the average value of the fragment length. The filament/matrix interface adhesion quality has been evaluated by determining the interfacial shear strength value (IFSS). According to Kelly and Tyson [10], the IFSS was estimated using equation (Eq. 2):

$$IFSS = \frac{\sigma_f(l_c) \cdot d}{2 \cdot l_c} \quad (2)$$

where *d* is the yarn diameter, l_c is the critical fragment length and $\sigma_r(l_c)$ is the yarn strength at a length equal to the critical yarn length. Because of the small l_c values, the yarn strength at a length equal to the critical yarn length, σ_f (l_c), was calculated taking into account the Weibull parameters obtained with tensile tests on flax yarns of 40 mm (L_0) length. As reported in literature [11-12], the $\sigma_f(l_c)$ value may be obtained by applying the equation (Eq. 3) :

$$\sigma_f(l_c) = \sigma_f(L_0) \cdot \left(\frac{L_0}{l_c}\right)^{-\frac{1}{m}} \quad (3)$$

where L_0 is the gauge length used for tensile tests, l_c is the critical fragment length and *m* is the shape parameter of Weibull distribution.

2.3 Optical and FE-SEM observations

The flax yarn diameters and all the fragment length measurements were carried out by using a ZEISS Axio Imager optical microscope. The morphology of the single yarn composite fracture surfaces was investigated by a field-emission gun scanning electron microscope (JEOL JSM-7000F). All specimens were sputter coated with gold prior to FE-SEM observations.

2.4 Micro-CT apparatus

Image acquisition has been performed using an UltraTom CT scanner manufactured by RX Solutions (France). The system consists in a Hamamatsu open type microfocus X-ray tube operating at 20-100 kV / 0-200 µA, within a maximum power of 20 W. A 1.5 µm resolution has been used in this work, with an accelerating voltage of 50 kV and a beam current of 157 µA. This X-ray detector consists in an X-ray CsI scintillator screen which is settled on an amorphous silicon layer. For 3D reconstruction, X-ray images were acquired from 1120 rotation views over 360°. The reconstruction was performed using an algorithm based on the filtered back-projection procedure for Feldkamp cone beam geometry. The analysis of the micro-CT pictures has been performed by using the Avizo 9.0 software.

3. Results and discussion

At first the adhesion quality of the untreated flax yarn with both epoxy and vinylester matrices was analyzed. The two thermoset systems exhibited different results. The critical fragment lengths and the debonding lengths have been measured by optical microscopy (Fig. 1). Because of the heterogeneity of diameter values, the l_c/d and $l_{debonding}/d$ ratios have been calculated in order to compare normalized values (Table 1).

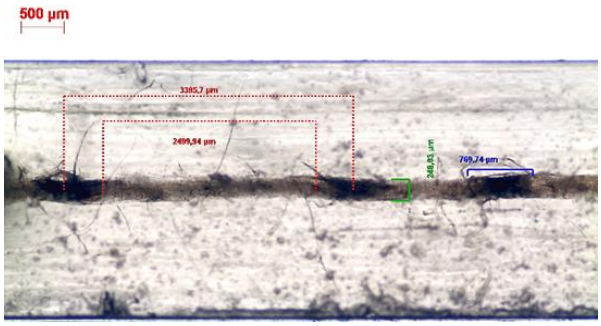

Figure 1. Optical micrograph of the fragmented flax yarn: measurement of the yarn diameter d, the fragment length l and the debonding length $l_{debonding}$.

Table 1. Critical fragment length and debonding length values for flax/epoxy and flax/vinylester single yarn composites.

Flax/Epoxy Resin	Yarn diameter d (μm)	Number of fragments	l_c/d	$l_{debonding}$ (μm)	$l_{debonding}/d$
EF_1	210 ± 35	8	12.18	504 ± 102	2.39
EF_2	222 ± 32	8	8.83	356 ± 155	1.61
EF_3	253 ± 43	7	12.35	460 ± 96	1.82
EF_4	247 ± 21	8	9.95	465 ± 9	1.88
EF_5	308 ± 25	5	12.04	446 ± 128	1.45
EF_6	250 ± 18	8	9.15	432 ± 137	1.73
Mean Value			10.75 ± 1.61	444 ± 49	1.81 ± 0.32
Flax/Vinylester Resin					
VF_1	238 ± 22	5	13.09	1466 ± 294	2.21
VF_2	281 ± 15	4	16.84	959 ± 252	2.39
VF_3	271 ± 33	6	12.37	599 ± 181	1.92
VF_4	316 ± 23	5	13.21	755 ± 181	2.03
VF_5	336 ± 39	4	14.78	648 ± 156	6.15
VF_6	273 ± 19	6	11.95	555 ± 301	3.40
Mean Value			13.7 ± 1.81	830 ± 343	3.02 ± 1.62

A larger number of fragments was found for flax yarn embedded in epoxy matrix. This system was characterized by critical fragment length values lower than those found in the case of vinylester resin. This indicates a better adhesion quality between flax yarn and epoxy matrix than the one observed with the vinylester matrix. Concerning the debonding length measurement, higher values have been found for the system constituted by flax yarn and vinylester matrix. As reported by Kim et al. [13], a large value of the debonding zone is typical for weak interfacial bonds. For this reason it is possible to assert the higher adhesion quality of flax yarn with the epoxy matrix. The interfacial shear strength value has been evaluated using Eq. 2. The IFSS values found for the untreated flax yarn reflect the results already found by comparing the critical fragment lengths. In fact, IFSS values of 19.39 MPa ± 3.76 MPa and 13.91 MPa ± 2.85 MPa were found for the untreated flax/epoxy and the untreated flax/vinylester composites, respectively. From these values, it is possible again to conclude that the flax yarn/epoxy system is characterized by a better interface quality than the flax/vinylester one. A morphological investigation of the fracture surface of the untreated flax yarn samples with epoxy and vinylester resins has then been performed using the FE-SEM. A yarn failure concentrated mainly in the peripheral zone of the yarn has been found (Fig. 2-A, Fig. 2-B).

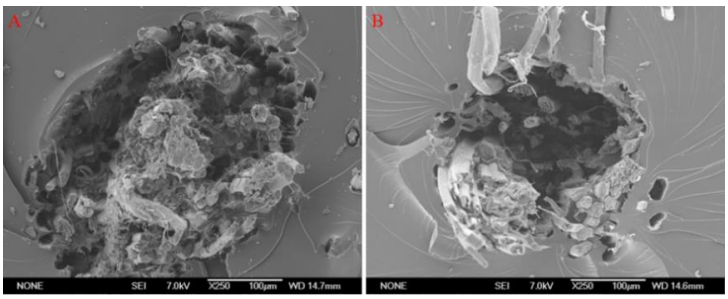

Figure 2. FE-SEM-micrographs showing the fracture surface for flax/epoxy (A) and flax/vinylester (B) single yarn composites.

This phenomenon is particularly evident for the flax/epoxy samples (Fig. 2-A), while conversely a partial tearing of the yarn was found for most of the vinylester samples. This different behavior can be considered as a further confirmation of the lower adhesion quality between the flax yarn and the vinylester matrix. A 3-D reconstruction of the breaking area of the untreated flax yarn has been performed using the AVIZO 9.0 software. The analysis carried out on both epoxy and vinylester samples has shown that the breakage of flax is mainly concentrated in the peripheral zone of the yarn (Fig. 3). This result is totally in accordance with what was observed by FE-SEM analysis on fracture surfaces (Fig. 2).

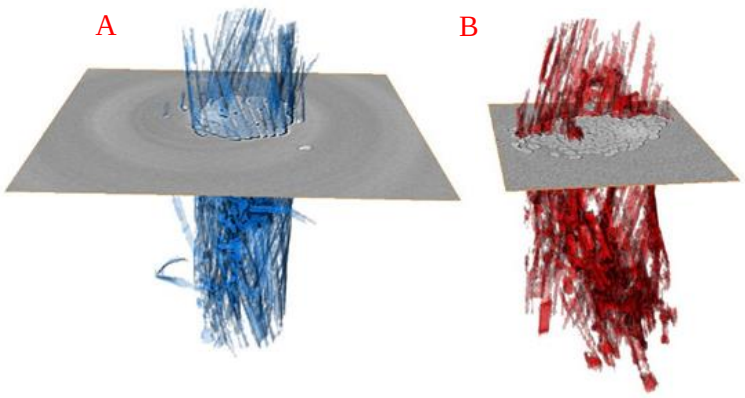

Figure 3. Volumetric reconstruction of the fracture zone for both flax/epoxy (A) and flax/vinylester (B) systems. The fracture zone is represented in blue and red for flax/epoxy and flax/vinylester samples, respectively.

With the aim of optimizing the fibre/matrix interface quality, two different treatments have also been tested: a plasma polymerization treatment and an enzymatic treatment. For the plasma treatment, a tetravinylsilane plasma (3.8 Pa, 10 W) was employed for 15 min. For the enzymatic treatment, a Peclyve EXG solution able to remove both pectine and hemicellulose content of flax fibres was used in a bath at the temperature of 50 °C. Fragmentation tests have then been carried out on epoxy samples made with treated yarns. The critical fragment lengths and the debonding lengths have been measured by optical microscopy, and IFSS values have been determined as for untreated yarns. Comparing the debonding length values, both enzymatically and plasma treated flax yarns have shown lower debonding length values than the untreated flax yarn. In particular, the best results were obtained for the flax yarn treated by the plasma polymerization process. Moreover, after the plasma polymer deposition process, samples showed a strong increase in the IFSS values. These results are promising concerning the use of the plasma polymerization process for improving the adhesion quality of flax yarn with the epoxy matrix.

4. Conclusions

The aim of the present work is to assess the adhesion quality of flax yarns with epoxy and vinylester polymer matrices. At first, a characterization of the interface properties of untreated flax yarn has been performed through fragmentation tests at yarn/matrix interface. A higher debonding length (by Micro-CT analysis) and lower number of fragments were detected for flax fibres embedded in a vinylester resin. Subsequently, an assessment of the effect of different physical (plasma treatment) and chemical (enzymatic) treatments on the adhesion properties of flax yarn with epoxy and vinylester matrices has been carried out. It was found that both treatments showed lower debonding length values compared to the unsized fibres with a better overall result offered by plasma treatment, thus suggesting its potential role in enhancing the mechanical properties of the resulting composites.

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