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Interfacial properties of flax fibre–epoxy resin systems: Existence of a complex interphase

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ABSTRACT

The purpose of the present article is to evaluate the real fibre surface involved in the practical adhesion of a flax/epoxy system. The difference in practical adhesion evaluated by microbond tests between Hermes (τ_{app} = 22.5 ± 1.5 MPa) and Electra (τ_{app} = 13.2 ± 3.2 MPa) flax fibres varieties/epoxy systems could not be explained by their superficial surface chemistry evaluated by XPS. FTIR spectroscopy highlights a difference in biochemical composition and Laser Confocal microscopy evidences a resin penetration for the two flax fibres systems (1.7 ± 0.7 μm for Hermes and 2.2 ± 0.8 μm for Electra). Thus the effective surface or complex interphase will be by consequence the overall area where the resin and fibre are in contact, i.e. the entire area penetrated by resin.

1. Introduction

High specific mechanical properties coupled with a low environmental footprint can be reached especially with flax fibre as a reinforcement [1]. Plant fibres bring complexity because different interfaces can be found in plant fibre composites from stem cell-wall to components [2]. According to the typical surface definition, the flax fibre surface should be the outer layer, the primary cell wall. Results from typical surface characterisation such as wetting analysis [3], Atomic Force Microscope [4], FTIR or XPS [5] confirm the difficulty to properly characterise and to define the real surface of plant fibres due to heterogeneous surface chemistry.

Among recent published works [3,6–10] on plant fibre/matrix adhesion, Flax/PLLA, Flax/Polyester and Glass/Polyester have been highlighted to have comparable practical adhesion (interfacial shear strength (IFSS). Recently, Le Duigou et al. [11] have shown that wet aging an epoxy microdroplet on single flax fibre induces reduction of interfacial shear strength but IFSS remains almost constant around 10 MPa. Mechanisms which are responsible for durable bond strength between flax and epoxy are still open to discussion.

The purpose of the present article is to understand the real fibre surface involved in the practical adhesion of a flax/epoxy system. Two varieties of flax fibres are used for the analysis. First, a microbond test will evaluate the practical adhesion of different raw flax fibre/epoxy systems. Then, resin penetration inside the fibre cell-wall will be evaluated by Laser Confocal microscopy. Finally a different surface characterization method will be used in order to evaluate "superficial" surface (few nanometres) with X-ray Photoelectron Spectroscopy (XPS) FTIR spectroscopy coupled with PCA analysis to give information on "micro-volume" composition.

2. Materials and methods

2.1. Material

Flax fibres of Hermès and Electra varieties are used. They have been harvested in Normandy (France) in 2003 and 2007 respectively, where they have been dew retted to help fibre extraction. Hermes fibres have been scutched and hackled while Electra fibres have only been scutched. Single fibres were manually extracted and bonded to cardboard supports. The tensile properties of these fibres have been described previously [7,12] and show higher Young's modulus (E_{Hermes} = 67 ± 16 GPa; $E_{Electra}$ = 51 ± 15 GPa) and tensile strength (σ_{Hermes} = 1057 ± 462 MPa; $\sigma_{Electra}$ = 808 ± 342 - MPa) for Hermes fibres.

The thermoset resin was a DGEBA epoxy (AXSON Epolam 2020, with 32% by weight aliphatic amine hardener).

2.2. Practical adhesion: microbond bond test

Microbond samples and characterization are done following the same protocol as described elsewhere [11]. The apparent shear

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strength at debonding (τ_{app}) is calculated using (Eq. (1)) from Ref. [13].

$$\tau = \frac{F}{\text{Embedded surface}} \quad (1)$$

τ corresponds to either the apparent shear stress at debonding τ_{app} or the friction stress after debonding $\tau_{friction}$. F is either the debonding force or the friction force. The embedded surface area corresponds to the bonded area between the fibre and the matrix.

A complementary approach rarely used for debonding tests consists of using the Weibull probability distribution to describe the variability of interfacial shear strength of our different systems. This approach is based on the weakest link theory and assumes that only one kind of flaw leads to failure [14]. The Weibull probability is given by Eq. (2):

$$P_f = 1 - \exp\left(\left(-\left(\frac{\tau_{app}}{\tau_{app0}}\right)^m\right)\right) \quad (2)$$

where P_f is the probability of interfacial failure, τ_{app} is the interfacial shear strength, τ_{app0} is the Weibull scale parameter, m is the Weibull modulus or shape parameter. Weibull shape (m) and scale parameters are estimated by plotting the Weibull distribution (Eq. (3)):

$$\ln(-\ln(1-P_f)) = m\ln(\tau_{app}) - m\ln(\tau_{app0}) \quad (3)$$

2.3. Resin penetration quantification: Laser Confocal microscopy

The fibres were labelled by immersion in water based Acriflavine solution (10 mg/L) [15]. Rhodamine B is assumed to be chemically grafted to epoxy resin according to protocol found in the literature [16]. Then, Rhodamine B grafted epoxy is blended with labelled flax fibres inside a small plastic mould. Polymerization is performed at 65 °C for 14 h which is similar conditions than microdroplet formation. Finally careful surface polishing is done. Analysis with Confocal laser scanning microscopy (CLSM) is undertaken on a Zeiss LSM510 laser scanning microscope with a 40× 1.3 N.A. water immersion lens. Multitrack images were performed; Acriflavine (fibre) signal is observed by exciting at 477 nm (Ar laser) and by collecting emitted photons with a 505/550 bandpass emission filter; Rhodamine B (matrix) was excited at 543 nm (HeNe laser) and emission was monitored with a 585LP filter. The software used for image acquisition is LSM 510 – Confocor 2 software, version 3.2 (Zeiss). Digital images are recorded at 2048 × 2048 pixels resolution. Resin penetration is estimated on 40 samples by plotting the fluorescence intensity of the fibre and resin labelled across sections of the fibre cell-wall and evaluating the overlap of fibre and resin fluorescent signals.

2.4. Superficial surface analysis: X-ray Photoelectron Spectroscopy

XPS spectra are obtained with a SCIENTA SES-200 instrument equipped with a conventional hemispherical analyser. Typical setup for natural fibres are used [17].

2.5. Microvolume surface analysis: FT-IR spectroscopy

A Nicolet FT-IR spectrometer equipped with an ATR device having an *X–Y* movable stage was used for recording the absorption spectra of flax fibres. Ge ATR crystal was used with a single reflection. This allows the evanescent wave to probe depths ranging from 1 to 3 μm depending on the wavelength, 128 scans were acquired and added at 4 cm^{-1} resolution. The scan were centred, scaled and averaged with Multiplicative Signal Correction (MSC) before analysis with the principal component approach as a multivariate analysis (unscramble software 9.7, CAMO, Trondheim, Norway) [18]. The multivariate analysis is used here to enhance the formation of clusters and therefore to sort the samples.

3. Results

3.1. Characterization of practical adhesion: microbond tests

The maximum load is assumed to correspond to debonding while the constant force recorded after debonding is the friction force. The values of F_{max} are used to calculate the apparent shear strength at debonding (τ_{app}) [13] using Eq. (1).

Even if the debonding behaviour is globally similar (Fig. 1A), Hermes and Electra systems have different interfacial shear strengths with respectively τ_{app} (Hermes) = 22.5 ± 1.5 MPa and τ_{app} (Electra) = 13.2 ± 3.2 MPa. Inter-varieties variability of flax fibres due to genetic and environmental parameters during growing is well known for tensile tests and should now be taken into account for interfacial properties. Weakest link theory and Weibull plots are used to describe the interfacial failure statistic of Hermes and Electra flax fibres/epoxy systems. The plot in Weibull coordinates for Hermes and Electra systems have a different behaviour (Fig. 1B). Hermes/epoxy is composed of several linear segments whose slope is very close with overall R^2 equal to 0.96. The Electra system presents several slope failures which bring a lower correlation coefficient (R^2 = 0.91). Analysing the two plots presented in Fig. 1B shows that the Weibull modulus m of the two systems varies from a factor of 2, with the Weibull modulus for Hermes/epoxy equal to 8.8 whilst being 4.5 for Electra/epoxy. Such values are difficult to compare with literature as the use of Weibull statistics for microbond test analysis is rare. Basically, the Weibull

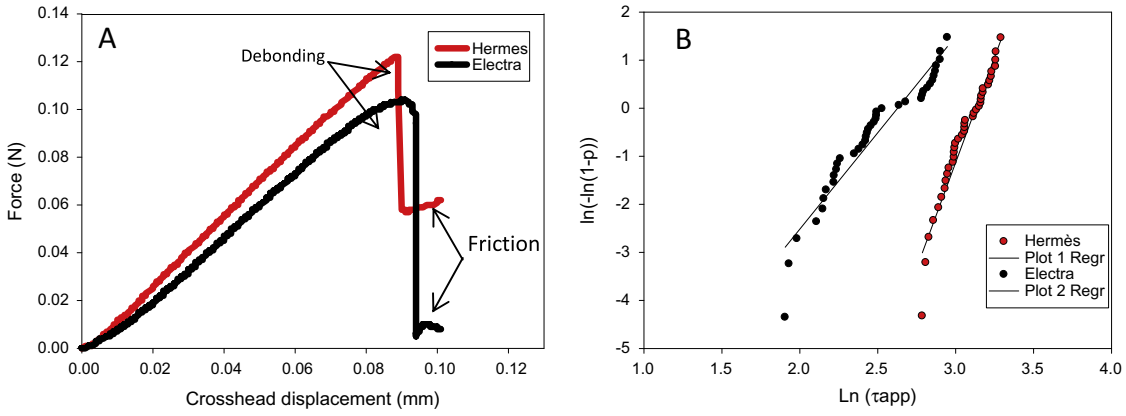

Fig. 1. (A) Typical mechanical behaviour observed during debonding test of flax (Hermes and Electra)/epoxy system. (B) Weibull probability plot for interfacial shear strength of Hermes and Electra systems.