Exploring durability of interfaces in flax fibre/epoxy micro-composites

Antoine Le Duigou [a,*], Peter Davies [b], Christophe Baley [a]

[a] LIMATB Laboratoire d'Ingénierie des matériaux de Bretagne, Equipe Polymères et Composites, Rue de Saint Maudé BP 92116, 56321 Lorient Cedex, France
[b] IFREMER Materials and Structures Group, Brest Centre, BP 70, 29280 Plouzané, France

ABSTRACT

The influence of wet aging on the behaviour of flax/epoxy micro-composites composed of single flax fibres embedded in epoxy micro-droplets has been studied. Interfacial shear strength has been examined by debonding the micro-droplets. The apparent interfacial shear strength decreases with immersion time in water, dropping rapidly during the first 15 min of immersion then stabilizing. Drying samples after short immersion periods allows recovery of properties, indicating a plasticization mechanism. For longer immersion times irreversible degradation is observed. Scanning electron microscopy reveals fibre surface peeling, indicating that an internal interface within the fibre is weaker than the fibre/matrix interface after aging. A simple descriptive model has been used to identify diffusion kinetics, with a critical diffusion time corresponding to a change in degradation mechanism.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The current environmental situation is encouraging designers to take environmental impact into account in addition to conventional criteria for material selection [1], such as mechanical properties, weight, and cost. The eco-design approach, which uses tools such as life cycle analysis, has shown the environmental advantages of natural fibre reinforcements [2,3] and biocomposites (natural fibre embedded in a biopolymer matrix) [4,5]. Le Duigou et al. [4] have shown that the lifetime of flax/Poly(L-Lactic) Acid biocomposites has a strong influence on their global environmental impact. Understanding the aging mechanisms of these materials is therefore of primary importance.

Aging in a humid environment affects the matrix, the fibres and the fibre/matrix interface of composite materials. The latter may control the long term durability, and Bordès [6] showed that the diffusion of water at a polymer/substrate interface may be much faster than that in the polymer alone. Kinloch [7] suggested that interface degradation may require a critical water level, while Cognard [8] proposed that water condensing at interfaces could result in osmotic pressure and lead to interface debonding.

Adherence is the sum of different contributions (chemical bonds, secondary interaction forces (van der Waals, acid/base, etc.), inter-diffusion, residual stresses, mechanical interlocking). These interactions control the load transfer between fibre and matrix and hence the global composite properties. The quality of the fibre/matrix interface also influences the water uptake of the composites. For example, Joseph et al. [9] showed that improved adherence between sisal fibres and polypropylene via chemical treatments reduced their weight gain due to water sorption, by reducing capillary water ingress.

Most published studies have focused on macroscopic properties, nevertheless understanding the direct interfacial damage mechanisms requires micromechanical studies (fragmentation, pull-out or micro-droplet debonding). These provide information on samples which are similar to unidirectional plies, at least with respect to the influence of the components in the unaged state [10]. Moreover, a micromechanical approach can be used to examine directly the effects of hygrothermal aging on the strength of the interfacial bond. For example, debonding of micro-droplets was used by Zinck and Gerard [11] who showed a decrease in critical strain energy release rate during the first 50 h of aging (60 °C and 98% RH) of glass/epoxy systems. Pandey et al. [12] showed a drop in apparent shear strength on carbon/epoxy composites, from 88 to 80 MPa after immersion in boiling water for 48 h. They explained this by radial stresses relaxation during immersion. Gaur and Miller [13] also noted a drop in the properties of glass/epoxy and Kevlar®/epoxy systems at 100 °C and 85% RH. These changes were completely recovered after drying for the Kevlar®/epoxy and partially recovered for the glass/epoxy. Gaur and Miller [13] also observed during immersion a 21% increase in post-debonding frictional stress due to the pressure exerted by matrix swelling.

Similarly, the aging mechanisms in natural fibre composites in water have mostly been studied at the macroscale [14–19]. The fibre–matrix interface is often cited as a privileged region for degradation, resulting in a decrease in global composite mechanical properties. However, very few publications describe direct measurement of Interfacial Shear Strength degradation of natural fibre/matrix systems during immersion.

* Corresponding author. Tel.: +33 2 97 87 45 86; fax: +33 2 97 8745 88.
E-mail address: antoine.le-duigou@univ-ubs.fr (A. Le Duigou).

The aim of this paper is to draw a baseline of knowledge on the interfacial degradation mechanism of a flax fibre/epoxy system thanks to direct measurement using micro-scale debond tests. This information will be useful to predict the lifetime of natural fibre composites in wet environments, both for mechanical design and in order to improve Life Cycle Analysis (LCA) calculations.

2. Materials and methods

2.1. Materials

Flax fibres of the Hermès variety (harvested in 2003) were used in this study; these have been extensively characterised in previous studies [20–22]. These fibres were taken from plants grown in France (Normandy), they were dew retted to help fibre extraction then scutched and hackled. It is important to note that no other treatment was applied to the fibres. Then, single fibres were manually extracted and adhesively bonded (Loctite Super glue) to rectangular aluminium supports (10×30 mm) with an elliptical window (L_{free} = 10 mm). Aluminium supports are used instead of cardboard supports to allow complete immersion of the sample without degradation of the support. The quality of the fibre/aluminium support bonding was checked after immersion and before characterisation. Furthermore each sample was checked by optical microscopy, to measure diameter ($d_{average}$ = 16.3 ± 3.5 μm) and to avoid multiple fibres and defects.

The thermoset resin for micro-droplet formation was a DGEBA epoxy (AXSON Epolam 2020, with 32% by weight aliphatic amine hardener). This was post cured at 65 °C for 14 h after polymerisation at room temperature to complete the crosslinking process [23]. This post-cure temperature was chosen to minimise fibre degradation caused by removal of water [24].

2.2. Debonding of micro-droplets

The droplets were placed on the flax fibres using a single glass fibre which had been dipped in the epoxy resin. Microbond specimens were then checked under the microscope to control the droplet geometry, length and height. Samples with defects (kink bands on the fibre or lack of symmetry of the droplet) were systematically rejected. Besides being symmetrical, microdroplets need to be smaller than 150 μm length otherwise the fibre will break. At least 20 specimens were tested for each test condition. Then the flax fibre with the epoxy microdroplet was mounted in the shearing device and continuously observed with a microscope. The fibre was pulled out of the droplet while the latter was constrained by the knife edges. The loading rate during debonding was 0.1 mm/min.

The drying kinetics of this geometry of fibre/polymer system are complex due to their small volume. Samples were removed from water just before testing, and the test lasted a few minutes in a controlled environment (23 °C and RH = 50%). It was therefore assumed that drying was negligible during testing.

Force–displacement plots were recorded for each specimen, in order to determine the debonding force and the friction force. Fig. 1 shows a typical plot for an epoxy microdroplet on a flax fibre.

The initial behaviour is quite linear as elastic energy accumulates up to a sudden drop in force. The maximum load corresponds to debonding. The stored energy is dissipated in the creation of an interfacial crack. The load does not drop to zero as frictional forces are present (Fig. 1). The values of F_{max} and $F_{friction}$ are used to calculate respectively the apparent shear strength by evaluating the linear regression slope of the plot of forces versus debonded area. The validity of this approach was checked using a method
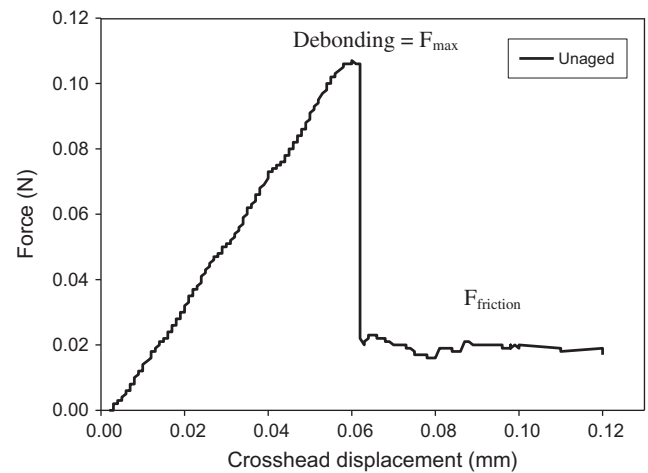

Fig. 1. Typical debonding curve for unaged flax/epoxy specimen.

proposed by Miller [25] (Eq. (1)) which assumes uniform distribution of stress along the fibre/matrix interface:

$$\tau = \frac{F}{\text{Embedded surface}} \tag{1}$$

where τ corresponds to either the apparent shear strength τ_{app} or the friction strength $\tau_{friction}$. F is either the debonding force or the friction force. The embedded surface area corresponds to the bonded area between the fibre and matrix and is calculated by multiplying the perimeter of the fibre (assuming a circular shape) by the microdroplet length.

2.3. Aging conditions

Flax fibre/epoxy microdroplet samples were immerged in a glass container containing de-ionised water at room temperature. A set of specimens was tested immediately after removal from water after the following immersion periods: 15 min, 840 min, 5160 min and 8100 min. A second set was immersed for the same periods but after removal from water these were dried under vacuum for 1 week at room temperature (T = 23 °C and RH = 50%). Given the small matrix volume it is assumed that all the absorbed water was removed.

2.4. Scanning Electron Microscope (SEM)

All the debond specimens (20 for each immersion time) were examined in the SEM (Jeol JSM 6460 LV) after testing in order to observe damage and debonding mechanisms. The specimens were coated with a thin gold-palladium layer to avoid charging.

3. Results and discussion

3.1. Evolution of interfacial shear strength with aging time

Fig. 2A and B shows a flax/epoxy micro-droplet system which has been subjected to immersion for 8100 min without debonding. No damage of the fibre/matrix interface is visible at this scale which indicates the validity of the following microbond tests.

Fig. 3A shows typical plots from debonding tests on flax fibre/epoxy samples after different immersion times in de-ionised water (the friction part of the curve has been shortened for clarity). Fig. 3B shows how the maximum force values recorded at debonding evolve with bonded surface area between fibre and matrix, for all the immersion conditions, Fig. 3C shows the friction force plots.