ADHESION BETWEEN A FLAX FIBER AND BIOBASED THERMOSET MATRIX

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Keywords: adhesion, flax fibre, biobased, thermoset

1 General introduction

Among the thermoset resins, epoxy and polyester resins are the most commonly used for composites which require high mechanical performances. The main drawbacks for the using of thermoset resins are their uneasy recyclability and the toxicity of their constituents and solvants. During the epoxy resin common synthesis, an epoxy precursor reacts with an amino or acid anhydride hardener. The traditional epoxy precursor in the industry is the Bisphenol A diglycidyl ether (DGEBA) (Fig. 1), obtained from Bisphenol A (BPA), a toxic component for human and environment, and epichlorhydrine.

![Fig. 1. DGEBA chemical formula.](image)

Epichlorhydrine and BPA come traditionally from petroleum resources. 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 (amino or anhydride) hardeners. Epichlorhydrine can be produced from biosourced glycerol. Solvay set in place in 2007 the EPICEROL™ process [1] which uses this technology. Dow Epoxy, Spolchemie and Sicomin with its Greenpoxy 55® use biobased epichlorhydrine for epoxy resin production as well.

![Fig. 2. Triglyceride molecule [4].](image)

Now, most of the major resins producer has a “green” range of resins. The bio-content is not always measured according to the same method, though. The American standard ASTM D 6866-12 [5] allows to determine the renewable carbon content. It is based on the carbon dating method. Another way to quantify the renewable content is to give a weight percentage of the biocontent in the final resin. Generally speaking, in order to guaranty the optimal performances for composites, a good adhesion between fiber and matrix is required. The adhesion between polymers and vegetal fibers has often been criticized and numerous treatments have been tested in the literature to improve the fiber/matrix interface [6][7]. The aim of this article is to measure the adhesion between flax fibers and partially biobased epoxy resins available on the market, and to

90%. Like epichlorhydrine, biobased BPA is still harmful (CMR 2 product). Epoxidiased oils can be good candidates as epoxy precursors, which would avoid the use of DGEBA. Since 1996, natural triglyceride oils have been used as a basis for polymers, adhesives, and composite materials [2][3]. These oils can be derived from plant or animal sources, and are made up mainly with triglyceride molecules, whose structure is presented in Fig. 2. Triglycerides are composed of three fatty acids joined at a glycerol juncture. Most common oils contain fatty acids that vary from 14 to 22 carbons in length, with 0 to 3 double bonds per fatty acid [4]. The epoxidiased triglyceride oil can react with an amino or anhydride hardener to produce an epoxy matrix resin.
compare the results to those obtained for the petrochemical commonly used equivalent. The adhesion between the resins and a flax fiber will be investigated at the microscopic scale via the debonding test. As the quality of adhesion between fiber and matrix has an influence on the in-plane shear resistance, in plane shear test will be carried out on ±45 laminates composites at the macroscopic scale. The results of adhesion at the both scales will be linked together.

2 Material and methods

2.1 Flax fibers

Two different batches of fibers have been considered. The flax fibers used for the debonding test belong to the Melina variety (harvested in 2009) and were supplied by La Calira company (Picardie, France). They were dew retted to help fibre extraction then scutched and hackled. No further treatment was applied to the fibers. The second batch is used for making the composites samples for the in-plane shear test. It consists in flax fibers in the form of layers of two unidirectional tapes of untwisted yarns in a 0/90 configuration, stitched together with cotton thread, supplied by C.R.S.T (France) with a weight of 500 g/m². The fibres were grown in France and had been dew retted before stripping and combing.

2.2 Epoxy matrix

The study focuses on commercialised epoxy matrix. Given that each main resin producer has its green range of matrix, only matrices with a renewable carbon content superior to 50% have been retained as “partially biobased matrix”. A petrochemical reference has also been selected. The studied matrix and their characteristics (biocontent, origin of biocontent and curing specifications) are gathered in the Tab. 1.

2.3 Matrix tensile test

Tensile test on the matrix have been carried out on the apparatus MTS Synergie RT1000 (MTS, Eden Prairie, MN, USA). The laboratory atmosphere is controlled at a temperature of 23°C and a humidity of 48%. Tensile testing followed ISO 527 instructions. The loading speed was 2 mm/min. Extensometer HTE was used with a nominal length of 49.7 mm. The tests were carried out at least five times for each specimen and the results were averaged arithmetically.

2.4 Samples preparation for in-plane shear test

Specimens for in-plane shear were prepared according to ASTM D3518 [8] with the different matrices reinforced by (±45) flax layers. Volumic fiber content is around 24%. The shear test standard requires a [45/-45]ns stacking sequence with 2 < n < 4, and at least 8 reinforcement layers to limit tension-flexion coupling [9] and increase the interlaminar area. Laminates were made with 8 reinforcement layers under thermo-compression and rectangular coupons were milled with the following dimensions: (25 x 180 x 3) mm³.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Biocontent</th>
<th>Origin of biocontent</th>
<th>Curing specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM D6866</td>
<td>Weigth percentage</td>
<td></td>
</tr>
<tr>
<td>Petro</td>
<td>Petrochemical</td>
<td>-</td>
<td>2h at 120°C</td>
</tr>
<tr>
<td>Biobased A</td>
<td>55±2</td>
<td>Biobased epichlorhydrine</td>
<td>24h at Tamb + 24h at 40°C</td>
</tr>
<tr>
<td>Biobased B</td>
<td>-</td>
<td>50-55</td>
<td>2h at 80°C</td>
</tr>
</tbody>
</table>

Tab. 1. Studied epoxy matrix.
2.5 Density and fibers fraction in composites

Density of matrices and composites is measured with MS-DNY-54 Toledo Mettler scales. By weighing the sample in air and in ethanol, the density can be deduced by the calculation (1).

\[
\rho_{\text{sample}} = \frac{M_{\text{air}} \rho_{\text{air}} - M_{\text{ethanol}}}{M_{\text{air}} - M_{\text{ethanol}}} + \rho_{\text{ethanol}} \tag{1}
\]

Volumic fibers content is deduced from density according to the equation (2).

\[
V_f = \frac{\rho_{\text{composite}} - \rho_{\text{matrix}}}{\rho_{\text{fiber}} - \rho_{\text{matrix}}} \tag{2}
\]

An observation of the sections showed no significant porosities.

2.6 Debonding test

The droplets were placed on the flax fibres using a single glass fibre which had been dipped in the epoxy resin. Fibers with droplets are placed in an oven to cure according to the specifications of each resin supplier (see 2.2). Microbond specimens were then checked under the microscope to control the droplet geometry. 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 when loaded. Droplet length and height, and fiber diameter at both extremities are measured for the selected samples. Then the flax fibre with the epoxy microdroplet was mounted in the shearing device and continuously observed with a microscope. The fiber was pulled out of the droplet while the latter was constrained by the knife edges (Fig. 3). The loading rate during debonding was 0.1 mm/min.

Force–displacement plots were recorded for each specimen, in order to determine the debonding force and the friction force. At least 20 specimens were tested for each matrix. The interfacial shearing rupture mode is checked by an observation of the debonded droplet.

2.7 In-plane shear test

In-plane shear test has been carried out according to ASTM D 3518[8] on an Instron tensile testing machine equipped with a 50 kN capacity load cell, and loaded at a constant crosshead displacement rate of 2 mm/min up to rupture. The laboratory atmosphere is controlled at a temperature of 23°C and a humidity of 48%. A biaxial extensometer measured the sample width and thickness variation during the test. At least five samples have been tested for each matrix.

3 Results and discussion

3.1 Tensile mechanical performances of the matrix

Results of the tensile test are presented in the Fig. 4 and values of Young’s modulus, strength at break and strain at break are reported in the Tab. 2.

The best performances in terms of Young modulus and tensile strength are attributed to the petrochemical matrix. The Biobased A resin shows properties close to these ones of the petrochemical matrix. This result is not surprising because these both matrix are based on the same components,
except that the epichlorhydrine of the Biobased A resin is biobased. The Biobased B resin has a high vegetable oil content in its epoxy precursor. The position of the epoxy functions in epoxydised oils, in the middle of the fatty acids, makes them hard to react with for the hardener, because of the repulsion from the apolar carbon chains. On the contrary, the epoxy functions in the DGEBA are located at the extremities of the molecule and are easily accessible. This configuration explains the slow reticulation of the resins using vegetable oil, and their lower tridimensional network density. Biobased A resin might have vegetable oil in its composition, which could explain its slight lowest performances comparing with these of the petrochemical matrix. For each studied matrix, the tensile strain is between 3.1 and 3.2%, so higher than the flax fiber tensile strain (around 2%). This is a favorable condition for using flax fibers as reinforcement in composites made with these matrix.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>E (GPa)</th>
<th>σ (MPa)</th>
<th>A (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petro</td>
<td>3.3±0.0</td>
<td>77±3</td>
<td>3.1±0.6</td>
</tr>
<tr>
<td>Biobased A</td>
<td>2.8±0.1</td>
<td>52±0</td>
<td>3.1±0.2</td>
</tr>
<tr>
<td>Biobased B</td>
<td>1.4±0.1</td>
<td>19±1</td>
<td>3.2±0.6</td>
</tr>
</tbody>
</table>

Tab. 2. Tensile performances of the matrix

3.2 Adhesion at the microscopical scale

Epoxy resins are able to create strong chemical bondings with flax fibers. Indeed, vegetal fibers are mainly constituted of cellulose and hemicelluloses. These components have hydroxyls groups at their surface, which can link to amino and epoxy groups of the epoxy resins via hydrogen bond. The quantification of the fiber/matrix link corresponds to the adhesion measurement. The debonding test has been chosen here to determine the adhesion of the several flax/epoxy systems. Fig. 5 shows a typical debonding curve for an epoxy droplet on a flax fiber. The initial behaviour is quite linear as elastic energy accumulates up to a sudden drop in force. The maximum load corresponds to the debonding. The stored energy is dissipated in the creation of an interfacial crack. The residual force is due to frictional forces of the droplet sliding on the fiber. The value of the debonding force $F_{\text{max}}$ permits to calculate the interfacial shear strength (IFSS). The equation (3) describes how to calculate the IFSS according to the Miller method [12].

$$IFSS = \frac{F_{\text{max}}}{2\pi r L}$$

$r$ is the fiber radius at the droplet extremities, $L$ is the droplet length, and the hypothesis of a circular section for the fiber is taken.

The IFSS obtained for the several systems flax/epoxy are given in the Fig. 6.

![Fig. 5. debonding curve for a flax/epoxy system [11]](image)

A uniform distribution of the stress along the fiber/matrix interface is assumed.

![Fig. 6. IFSS of flax/epoxy systems from the debonding test.](image)

The flax/Biobased B system shows the highest IFSS (28.5 MPa). Then, the flax/Petro system and the flax/Biobased A system have lower values of IFSS, close one to each other (20.4 and 17 MPa respectively). The adhesion is strongly dependent of
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The chemical bonding which set up at the fiber/matrix interface. Thus, matrix components have a straight influence on the microscopical adhesion. For both Petro and Biobased A resins, components are similar, so unsurprisingly their adhesions on the same flax fiber are in the same range. The Biobased B resin supplier underlines the high hydroxyle groups content in its resin. Hydrogen bonds between hydroxyle groups from the matrix with these of the fiber can in part explain the high adhesion obtained for the flax/Biobased B system.

Tab. 3 presents the results of this study amongst data from the literature, which have been established with the same device in the same laboratory.

<table>
<thead>
<tr>
<th>Fiber/matrix system</th>
<th>IFSS (MPa)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax/Petro</td>
<td>20.4±4.9</td>
<td>This study</td>
</tr>
<tr>
<td>Flax/Biobased A</td>
<td>17.0±5.0</td>
<td>This study</td>
</tr>
<tr>
<td>Flax/Biobased B</td>
<td>28.5±6.4</td>
<td>This study</td>
</tr>
<tr>
<td>Flax/EPOLAM 2020®</td>
<td>22.3±2.1</td>
<td>[13]</td>
</tr>
<tr>
<td>Flax/EPOLAM 2015®</td>
<td>16.1±0.8</td>
<td>[14]</td>
</tr>
<tr>
<td>Glass/EPOLAM 2020®</td>
<td>37.2±4.6</td>
<td>[13]</td>
</tr>
<tr>
<td>Glass/EPOLAM 2015®</td>
<td>29.3±2.4</td>
<td>[14]</td>
</tr>
</tbody>
</table>

Tab. 3. IFSS results from this study compared with literature

The IFSS value for the flax/Petro system is in accordance with the literature. The adhesion of the flax/epoxy system is slightly lower than the adhesion between glass and epoxy. However, man have to keep in mind the fact that flax fibers undergo no sizing treatment to improve the adhesion, unlike glass fibers. Microscopical adhesions of the flax/epoxy systems are satisfying, with petrochemical and partially biobased resins. Nevertheless, within a composite, other parameters, such as the shape factor of the reinforcement fiber, enter into account in the interface problem. Additional tests have been achieved to analyse the influence of the microscopic IFSS at the macroscopical scale, and to determine if a good microscopical adhesion is enough to guaranty a good interphase and to obtain performing composites.

3.3 In-plane shear test on ±45 laminates

The ±45 laminates have been cured according to the specifications of the resin suppliers they are made with (see 2.2), in order to be able to compare the results with the tensile performances of the matrix on one hand, and with the microscopical adhesion found with the debonding test on the other hand. The in-plane shear test is sensible to both the fiber/matrix interface and the matrix properties itself. This test provides shear strength τ_{12}, shear strain γ_{12} and shear modulus G_{12}. G_{12} is determined from the slope of the plot of shear stress versus shear strain for γ_{12} between 0 and 0.2%. Equations (4), (5), (6), give the different relations for calculating G_{12}, τ_{12} and γ_{12}:

\[
G_{12} = \frac{\tau_{12}}{\gamma_{12}} 
\]

(4)

\[
\tau_{12} = \frac{\sigma_x}{2} 
\]

(5)

\[
\gamma_{12} = (\epsilon_x^0 - \epsilon_y^0) 
\]

(6)

σ_x is the applied strength.

Under loading, the fibers rotate and the rotation reaches 1° for an axial strain of 2% [15]. According to the ASTM D3518 standard [8], if the shear strain is below 5% the shear stress can be taken at the maximum value: σ_x = σ_{max}. If not, the shear stress corresponding to a 5% shear strain is used: σ_x = σ_y=5%.

For unreinforced matrix, shear properties are calculated from tensile data according to the equations (7) and (8):

\[
G_{12} = \frac{E}{2(1+\nu)} 
\]

(7)

\[
\tau_{12} = \frac{\sigma}{3} 
\]

(8)

Volumic fibers content (VF) for the composites manufactured with the several matrix for the in-plane shear test are given in the Tab. 4. They are found in the same range (24-25%) so the results can be compared.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>VF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petro</td>
<td>24</td>
</tr>
<tr>
<td>Biobased A</td>
<td>24</td>
</tr>
<tr>
<td>Biobased B</td>
<td>25</td>
</tr>
</tbody>
</table>

Tab. 4. Volumic fibers content for composites laminates used for in-plane shear test.
Many studies ([16][17][18][19]) found that the higher the fiber/matrix bonding at the microscopical scale (high IFSS), the greater the macroscopical properties for the corresponding composites. The improving of the macroscopical properties would not be proportional to the improving of the microscopical IFSS though. Tab. 5 presents the results obtained in this study comparing with the literature data. Flax/epoxy systems results are in accordance with the literature. These values are lower than the shear performances of glass/epoxy composites.

Shear performances of the laminates manufactured with the different matrix are exhibited on the Fig. 7. The previous hierarchy given on the matrix by the tensile test is found: shear modulus of the composites made with petrochemical and Biobased A matrix are close, and the shear strength of the composite made with the Biobased A matrix is inferior to this of the petrochemical composite. The composite flax/Biobased B has the lowest shear modulus and shear strength. The poor Biobased B rigidity explains the low shear modulus. The flax/Biobased B system had a high IFSS (almost 50% higher than for the two other systems) at the microscopical scale, but this superiority is not kept at the macroscopical scale.

The fiber/matrix bonding would not be the decisive criterion for good macroscopical shear properties, but matrix intrinsic properties would prevail. This phenomenon has already be observed by Le Duigou et al [15] on a PLLA matrix which underwent several way of cooling: at the composite scale the matrix properties and morphology appear to dominate those of the interface. Even if the PLLA is a thermoplastic matrix, its mechanical properties close to epoxy or polyester ones make possible the comparison.

<table>
<thead>
<tr>
<th>Fiber/matrix system</th>
<th>$\tau_{12}$ (MPa)</th>
<th>$G_{12}$ (MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite</td>
<td>Matrix</td>
<td>Composite</td>
<td>Matrix</td>
</tr>
<tr>
<td>Flax/Petro</td>
<td>48 ± 8</td>
<td>44</td>
<td>2405 ± 117</td>
</tr>
<tr>
<td>Flax/Biobased A</td>
<td>40 ± 9</td>
<td>30</td>
<td>2507 ± 215</td>
</tr>
<tr>
<td>Flax/Biobased B</td>
<td>36 ± 4</td>
<td>30</td>
<td>1443 ± 133</td>
</tr>
<tr>
<td>Flax/Epoxy</td>
<td>46 ± 2</td>
<td>-</td>
<td>1679 ± 121</td>
</tr>
<tr>
<td>Glass/Epoxy</td>
<td>52 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 5. In-plane shear performances of flax/epoxy composites from this study comparing with literature data.

Fig. 7. In-plane shear performances of flax/epoxy composites (a) shear modulus, (b) shear strength.
4 Conclusion

Adhesion on flax fibers of petrochemical or partially biobased epoxy resins has been investigated at both microscopical and macroscopical scales. At the microscopical scale, the debonding test highlighted a satisfying adhesion (high enough IFSS) for every flax/partially biobased epoxy system. Additional tests have been carried out to analyse the influence of the interfacial bonding at the macroscopical scale. Better macroscopical shear properties are not observed when microscopical IFSS is higher, as it could be expected. Intrinsic matrix properties would be most influent than the microscopical fiber/matrix bonding for the macroscopical shear properties of composites. This study highlights encouraging results for the use of partially biobased epoxy resins in composites, even if mechanical performances of these resins remain lower than these ones of their petrochemical equivalent.

References
