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# EFFECT OF POST CURING TEMPERATURE ON MECHANICAL PROPERTIES OF A FLAX FIBER REINFORCED EPOXY COMPOSITE

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## ABSTRACT

Achieving a complete curing of biocomposites without damaging fibers is very challenging. This study assesses the impact of processing upon the mechanical properties of a unidirectional flax reinforced epoxy composite and identifies which component (resin, reinforcement or interphase) is the most sensitive to post-curing at high temperature (100, 120 or 150°C).

Post-curing temperature had a limited impact on the composite mechanical behavior excepted at 150°C where ultimate stress and strain decreased drastically while the stabilized modulus slightly increases.

Post curing is responsible of a slight decrease of the matrix tensile properties attributed to the polymer oxidation but cannot explain on its own the evolution of the composite behavior. Interfacial adhesion played a minor role in the composite behavior probably due to its

intrinsic weakness. Finally, the flax fabric was highlighted to be the component most sensitive to thermal treatment thus governing the drop in the composite mechanical properties.

Keywords: A. Biocomposite; B. Post-curing; C. Mechanical properties; D. Flax fibers

## 1. INTRODUCTION

Nowadays, composites reinforced with synthetic fibers such as carbon or glass fibers (CFRP or GFRP) are commonly used in various industrial fields from automotive to aerospace in order to reduce the weight of the final pieces [1].

But glass and carbon fibers present some drawbacks (energetically expensive, made of non-renewable resources, or difficult to recycle) [2,3].

An interesting alternative to glass fibers is natural fibers such as flax, hemp, or wood fibers. Indeed, natural fibers are carbon neutral, come from a renewable source and can easily be biodegraded [4]. They also have a lower density leading to specific properties similar to those of glass fibers [5,6]. But natural fibers also present some drawbacks: a large variability of mechanical and physico-chemical properties depending on the period of harvesting, the stem location and the extraction method, their low durability because of their hydrophilicity, their sensitivity to high temperature leading to processing difficulties especially during post-curing of thermoset composites [7–13]. This sensibility to high temperature raises several questions in the industrial field: Can the same processing protocol be used for biocomposites? What happens if high temperatures are applied during process?

Indeed, GFRP are generally cured at a “low” temperature (between 60 and 100°C) and post cured at higher temperature around 150°C or more to complete the curing and reach the highest crosslinking rate and glass transition temperature possible [14,15]. A post-curing is also done to improve the modulus and strength of both the polymer and the composite and reduce the residual stresses. However, a post-cure can also lead to the thermo-oxidation of the

resin. Such curing and post-curing conditions could degrade natural fibers. Natural fibers mechanical properties are mainly dependent on their water content [9,16–18]. Post-curing at high temperature is likely to change the fiber water content and thus modify their mechanical behavior. Müssig and Haag mentioned that exposure of flax fibers at 120°C leads to loss of moisture and degradation of waxes [19]. Placet showed that the mechanical properties (rigidity and fatigue behavior) of natural fibers are affected by thermal treatment beyond 150°C [13]. It was assumed to be related to the degradation of the cellular walls. Gassan and Bledski showed that a thermal exposure between 170 and 210°C leads to a significant drop in tenacity up to 70% for 2 hours at 210°C [12]. The degradation of mechanical properties could also occur at lower temperature during drying for instance [20]. On the contrary Xue and al. reported that a thermal exposure between 170 and 180°C does not impact significantly the tensile properties of kenaf bast fibers if the exposure lasts less than one hour [21].

It appears from this quick overview that achieving a complete curing of biocomposites without damaging fibers is very challenging. But, most of the time, in order to substitute glass fibers by natural fibers in structural composites, a traditional curing and post-curing at high temperature, recommended in the resin datasheet, is applied and leads to composite with degraded mechanical properties. The main objective of this study is to assess the impact of such traditional processing upon the properties of a biocomposite based on epoxy resin and unidirectional flax fabrics. The motivation is to identify which component (resin, reinforcement or interphase) is the most sensitive to post-curing at high temperature thus determining the final functional properties of the materials.

## **2. EXPERIMENTAL**

### **2.1. Materials**

The epoxy resin (DER 332) was provided by Dow Chemicals (Midland, USA) with an epoxy equivalent weight of 170g/eq. Isophorone diamine (IPDA) from Sigma Aldrich (Saint-Louis, USA) with a functionality of 4 was used as hardener. The mixing of resin and hardener was carried out at a stoichiometric epoxy/amine ratio (80%wt DER 332 and 20%wt IPDA).

Quasi-unidirectional flax fabrics UD 360 have been supplied by Fibres Recherche Développement (Troyes, France). Its areal weight is 360g/m<sup>2</sup> (weft: 330g/m<sup>2</sup>; warp: 30g/m<sup>2</sup>) and its thickness is 0.4mm.

## **2.2. Preparation of composites**

The composites were manufactured using a vacuum infusion process in controlled atmosphere (50%RH and 23°C). The resin was heated at 40°C to obtain a viscosity (of 120P/s) compatible with the vacuum infusion process and then mixed with the hardener during 3 minutes at 400rpm before the infusion. Four plies of fibers (300 x 300mm<sup>2</sup>) oriented in the weft direction were infused at a constant pressure of 100 mbar during 30 minutes. The composite was then cured at 80°C for 24h (NoPC). Three post-curing cycles were studied: 2 hours at 100°C (PC100), 120°C (PC120) or 150°C (PC150). Resulting composites contain 30%vol of fibers. Composite plates (300 x 300 x 3mm<sup>3</sup>) were then cut into various size samples and stored at 23°C and 50%RH according to ISO 291 and ASTM D618.

## **2.3. Characterization**

### **2.3.1 Differential Scanning Calorimetry (DSC)**

A PYRIS Diamond DSC from Perkin Elmer was used to assess the evolution of the glass transition temperature and the crosslinking rate of the composites. Samples between 10 and 15mg were tested in aluminum pans with holes. The purge gas was nitrogen (at 20L/min). The heating program consists of a first step of 3 minutes at 20°C followed by a heating step at

10°C/min from 20 to 200°C. The samples were then cooled at 10°C/min to 20°C and heated again following the same heating program.

To determine the crosslinking rate, uncured resin samples were analyzed following the usual thermal program. The DSC curves (Fig.1) showed an exothermic peak leading to the total curing enthalpy of the system ( $\Delta H_{total}$ , crosslinking rate of 100%). For the cured samples (NoPC, PC100, PC120 and PC150), the Heat Flow Vs. Temperature curves (Fig.2) showed an endothermic peak ( $\Delta H_{peak}$ , relaxation enthalpy) due to the cure at 80°C (NoPC) or the post-curing at 100 and 120°C (PC100 and PC120). The DSC curves for PC150 (Fig.2) showed no endothermic peak but a clear glass transition temperature. A simple cross-multiplication allowed us to calculate the composite crosslinking rate following the equation 1. The total enthalpy of curing ( $\Delta H_{total}$ ) and the various relaxation enthalpies are shown in Table 1.

$$X = \frac{\Delta H_{total} - \Delta H_{peak}}{\Delta H_{total}} \times 100 \quad (\text{Eq. 1})$$

### 2.3.2 Thermo-Gravimetric Analysis (TGA)

A Setaram (SETSYS evolution model) TGA device was used to assess the weight loss during different heating programs. Sample between 10 and 15mg were tested in ceramic crucibles. The purge gas was nitrogen (at 20L/min). The basic heating program consists of a first step of 20 minutes at 20°C followed by a heating step at 10°C/min from 20 to 900°C. The curing/post-curing cycles were also tested on the fibers: 24 hours at 80°C followed by 2 hours at 100°C, 120°C or 150°C to assess to possible weight loss during the processes.

**Table 1 – Total reaction enthalpy for the system DGEBA + IPDA and post relaxation enthalpies for NoPC, PC100, PC120 and PC150**

100% cured (DSC)	NoPC	PC100	PC120	PC150
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Enthalpy (J/g)	394	31	24	12	-
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### 2.3.3 Gas pycnometer

A Micromeritics gas pycnometer (AccuPyc 1330 model) with helium was used to determine the density of the different composites at room temperature. Series of 4 samples (between 0.7 and 2g) of NoPC, PC100, PC120 and PC150 were tested.

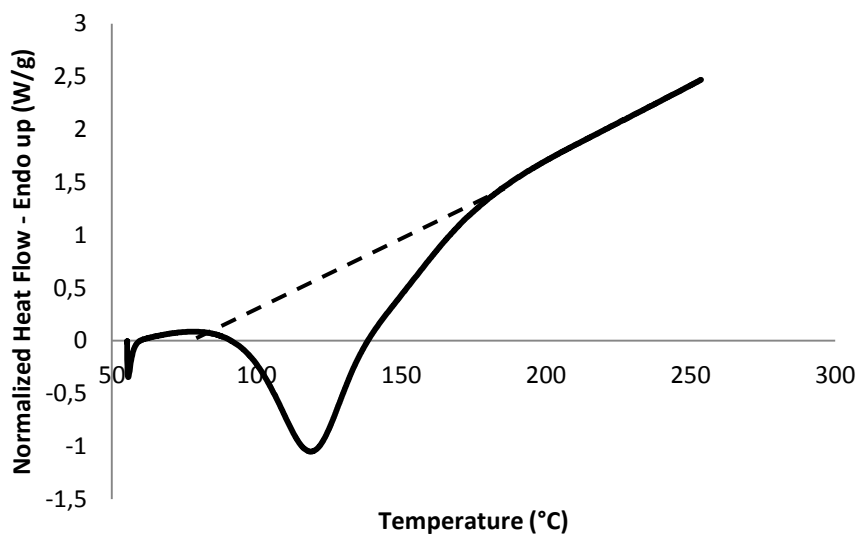


Figure 1 : DSC Curve for the system DGEBA - IPDA (cured 100%)

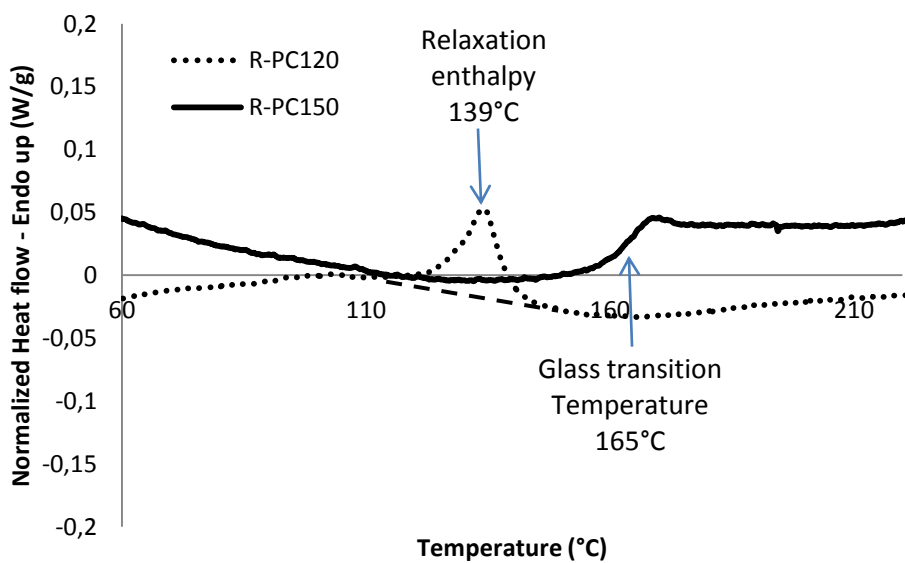


Figure 2 : DSC curves for R-PC120 (with relaxation enthalpy) and for R-PC152 (without)

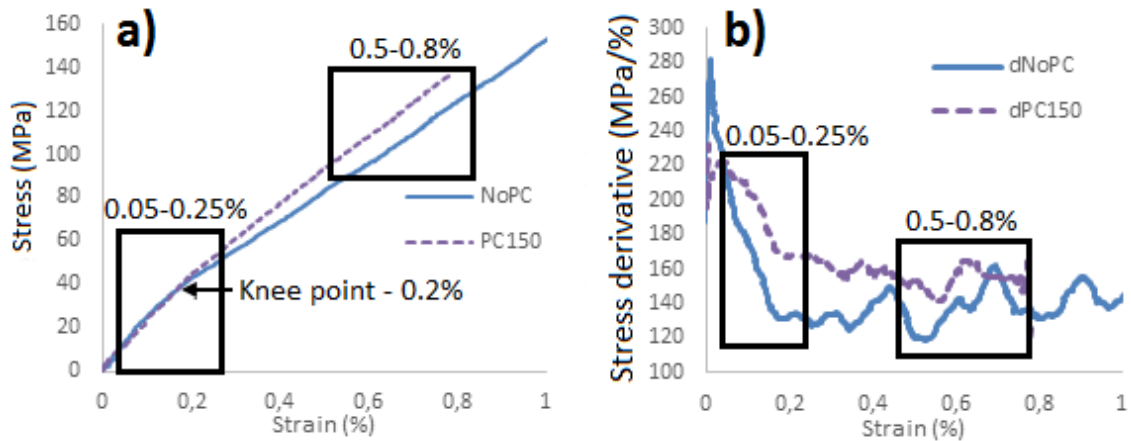
### 2.3.4 Uniaxial tensile tests

#### *Composites and resin*

Uniaxial tensile tests were performed on a MTS testing machine (model Criterion C45.105) equipped with a 100kN load cell. The tests were performed at a constant displacement rate of 1 mm/min. The deformation was measured using a MTS laser extensometer (Model LX500) with a precision of 1 $\mu$ m. Sample dimensions are 250 x 25 x 3 mm<sup>3</sup> for the composites (following NF EN ISO 527 standard) and 110 x 13 x 4 mm<sup>3</sup> for the resin. Series of 4 samples of NoPC, PC100, PC120 and PC150 were tested for the composite and series of 4 samples of R-NoPC, R-PC100, R-PC120 and R-PC150 were tested for the resin.

According to NF EN ISO 527-4 standard, Young modulus is obtained by linear regression between a strain of 0.05 and 0.25%. However, the NF EN ISO 527-4 standard is not adapted to bio-composites because of their bilinear responses in the range rather than the linear behavior assumed in the standard [9]. This bilinear behavior can be attributed to a reorientation of the cellular fibrils. There is a transition in the slope between 0.2 and 0.3% called a “knee-point” leading to incorrect modulus calculations (Fig. 3a) [22–24]. To overcome this issue, the modulus was calculated according to NF EN ISO 527-4 standard but also at higher strain between 0.5 and 0.8% leading to a stabilized modulus (Fig. 3b).





**Figure 3 – Strain-Tensile strength curves a) and Tangent Modulus b) for NoPC and PC150**

### *Flax fabrics*

Tensile tests were carried out on flax fabrics using a Zwick testing machine (TH010 model) with a loading cell of 10kN. The tests were performed at a constant displacement rate of 1 mm/min. Samples were 50mm large with a length ranging from 10 to 200mm to assess different modes of breaking (neat breaking and disentanglement). Series of 3 specimens per length were tested. Some fabrics were previously heated 24h at 80°C (F-No PC) and then 2h at various temperatures (F-PC100, F-PC120 and F-PC150) in order to simulate the curing process used to prepare the corresponding composites. The stiffness of the sample was determined using a linear regression on the linear part of the load-strain curves obtained.

#### 2.3.5 Interlaminar Shear Strength (ILSS) tests

Following the NF EN ISO 14130 standard, ILSS tests were conducted on a Zwick testing-machine (TH010 model) equipped with a 2.5kN load cell; the constant displacement rate was 1mm/min. The distance between the bending supports  $L$  was 15mm. The length  $l$ , width  $b$  and thickness  $h$  of specimens were respectively 30, 15 and 3mm. The interlaminar shear strength was calculated from equation 2 and the maximal tensile stress from equation 3, where  $F$  is the force applied to break the samples.

$$\tau_{ILSS} = \frac{3F}{4bh} \quad (\text{Eq. 2})$$

$$\sigma_{max \text{ tensile stress}} = \frac{4 F L}{3 b h^2} \quad (\text{Eq. 3})$$

### 2.3.6 Scanning electron microscopy (SEM)

Images of fractured cross-sections or of polished sections were acquired with an environmental scanning electron microscope (FEI Quanta 200). Samples were metallized with carbon in high vacuum to stabilize them during the analysis. The micrographs were then obtained under high vacuum at a voltage of 15kV, a working distance of 10mm and a 100 to 5000 magnification.

## 3. RESULTS AND DISCUSSION

### 3.1. Influence of post-curing on composite properties

#### 3.1.1 Evolution of the glass transition temperature and density

Table 2 shows that an increase of the post-curing temperature leads to an increase in the glass transition temperature measured during the first heating ramp from 115°C for NoPC to 167°C for PC 150. This phenomenon is due to the increase of the crosslinking rate of the composite. Indeed, the higher the process temperature is, the higher the crosslinking rate and the glass transition temperature will be. The post-curing of 2 hours at 150°C leads to a fully crosslinked resin with a maximum glass transition temperature of 167°C. For all other post-curing conditions, the crosslinking is incomplete and a second heating ramp allows increasing further the glass transition temperature.

**Table 2 – Glass transition temperature of the various composites**

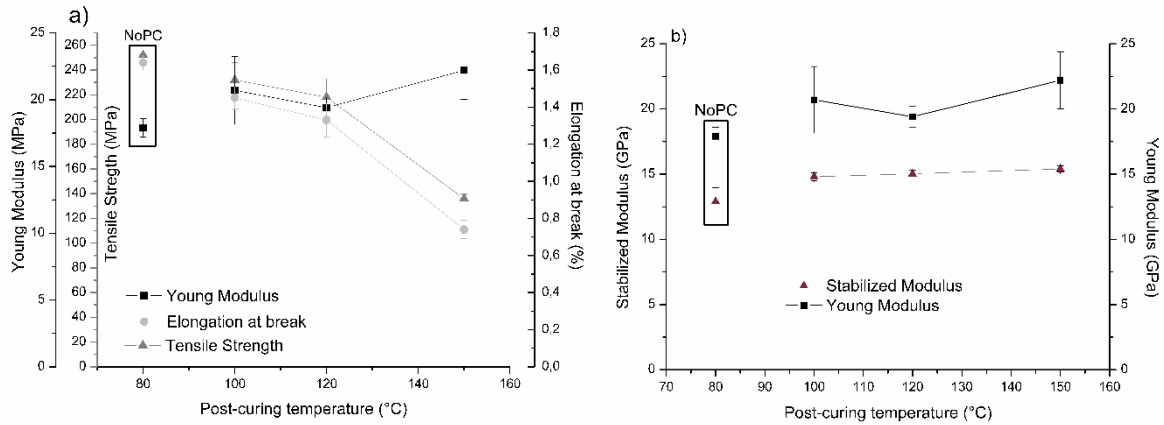
Sample	NoPC	PC100	PC120	PC150
1st temperature ramp (20°C – 200°C)	115°C	127°C	145°C	167°C
2nd temperature ramp (20°C – 200°C)	158°C	161°C	162°C	167°C

NoPC samples have a density of  $1.276\text{g/cm}^3$ . When the post-curing temperature increases, the composite density decreases progressively with a maximum decrease of 0.82% for PC150 ( $d_{\text{PC100}} = 1.270\text{g/cm}^3$ ,  $d_{\text{PC120}} = 1.266\text{g/cm}^3$  and  $d_{\text{PC150}} = 1.262\text{g/cm}^3$ ). Crosslinking rate, glass transition temperature and density are all related to the curing/post-curing temperature. The higher the glass transition temperature is, the lower the composite density will be (because of the resin density) [25–27]. The post-curing increases the crosslinking rate leading to less free ends. A re-arrangement of the molecular chains causes a variation of the samples specific volume (free volume + occupied volume) and thus a decrease of the density.

### 3.1.2 Tensile strength tests

The tensile strength of the non-post-cured (NoPC) and post-cured (PC100, PC120 and PC150) composites is shown on Figure 4a.

A decrease of the tensile strength from 252MPa for NoPC to 136MPa for PC150 is observed when the post-curing temperature increases. The higher the temperature of post-curing is, the lower the maximal stress is with a maximal decrease of 46% for the highest temperature. The decrease in tensile strength is particularly significant when post-curing temperature increases from 120 to 150°C with a relative variation of 40% between these two temperatures. A decrease of tensile strength despite a higher crosslinking rate evidences that one (or both) of the composite components is modified during post-curing.



**Figure 4 – a) Tensile strength (MPa), elongation at break (%) and Young Modulus (GPa) of the composites post-cured at 100, 120 and 150°C and b) comparison between the Young modulus (GPa) and the stabilized modulus (GPa)**

As shown in Figure 4a, the elongation at break (%) follows the same tendency. A significant decrease is observed for PC150 with an elongation at break of 0.74% (versus 1.64%, 1.45% and 1.33% for NoPC, PC100 and PC120 respectively). This may be explained by the modification of the resin which is more brittle when crosslinking rate is higher (see 3.2.1).

Bensadoun and al. studied epoxy composites reinforced with quasi-UD and UD flax fibers with a tensile modulus (calculated between 0.3 and 0.5% strain) of 15.9GPa and 20GPa respectively. Those composites had a fiber volume fraction of 40% and were manufactured using Resin Transfer Moulding [23]. NoPC samples have a stabilized modulus of 12.9GPa (between 0.5% and 0.8% strain) for a composite with a fiber volume fraction of 30%. Using the rule of mixtures, this modulus would be of 16.4GPa for a composite with a fiber volume fraction of 40%.

Baley and al. studied a flax/epoxy composite with a fiber volume fraction of 40% and manufactured by compression molding after wet impregnation of the fibers. The studied composites had an axial modulus (between 0.05 and 0.25% strain) of  $22.5 \pm 1.51$  GPa [20]. NoPC samples have a modulus between 0.05 and 0.25% strain of 17.9GPa for a fiber volume

fraction of 30%. Using the rule of mixture, this composite would have a modulus of 23.06GPa for a fiber volume fraction of 40%.

Many factors can affect the mechanical properties of a composite (type of flax and epoxy resin used, manufacturing process, ...). However, the values obtained for NoPC are comparable to the ones obtained by Bensadoun's and Baley's composites allowing to position our values in an acceptable range of modulus for an epoxy resin reinforced with flax fibers.

Figure 4a also shows the Young modulus for all composites according to NF EN ISO 527-4 standard. Despite the high standard deviations, the Young's modulus tends to increase when the temperature of post-curing increases from  $17.9 \pm 0.68$  GPa for NoPC to  $22.2 \pm 2.18$  GPa for PC150. This trend is also followed by the stabilized modulus which is 28% lower and more reproducible (Figure 4b). We observe a decrease of the elongation at break and the failure tensile strength while the modulus increases meaning that the composite is more brittle.

### **3.2. Influence of post-curing on the composite components**

In order to understand the behavior modifications of the composite when a post-cure is carried out, each component of the composite (resin, fibers and interface) was studied separately.

#### **3.2.1 Post curing of the epoxy resin**

##### ***Evolution of the glass transition temperature***

As shown in Table 3, 24 hours of curing at 80°C leads to a resin exhibiting a 92% crosslinking rate and a  $T_g$  of 121°C. The resin follows the same trend as the composite. When the post-curing temperature increases, an increase of  $T_g$  is also observed with a maximal value of 165°C for the resin post-cured 2 hours at 150°C. This trend was expected since the aim of

post-curing is to obtain a 100% crosslinking rate. After post-curing the molecular mobility within the resin is reduced, leading to a higher  $T_g$ .

**Table 3 – Glass transition temperatures and crosslinking rate of the resin**

Sample	R-NoPC	R-PC100	R-PC120	R-PC150
<b>T<sub>g</sub> (°C) (1st heating ramp)</b>	121°C	123°C	139°C	165°C
<b>T<sub>g</sub> (°C) (2nd heating ramp)</b>	165°C	162°C	163°C	165°C
<b>Cross-linking rate (%)</b>	92	94	97	100

It has been reported that the composite  $T_g$  (Table 2) may be slightly lower than the resin  $T_g$  (Table 3) due to the disruption of the resin network by the incorporation of fibers that could either absorb the amine hardener in the interface region or generate non cellulosic materials that migrate into the resin [28]. But an opposite phenomenon is observed when a post-cure is carried out at 100, 120 or 150°C because the composite  $T_g$  is higher than the resin  $T_g$ . This could be explained by a change in specific heat or thermal conductivity when fibers are introduced [29,30].

#### ***Tensile tests***

A decrease of the Young modulus (Table 4) is observed when a post-cure is realized on the samples with a maximal drop of 15% for R-PC150. This decrease could be explained by a change of resin density that varied from 1.276g/cm<sup>3</sup> for NoPC to 1.262g/cm<sup>3</sup> for PC150. However, no significant modification of the modulus was observed when the post-curing temperature increases (or the phenomenon is concealed by the high standard deviation of the results). Table 4 also shows the same trend (high standard deviation around an average strain of 3%) regarding the resin elongation at break after post-curing.

**Table 4 – Young Modulus (GPa), Maximal stress (MPa) and strain (%) of the epoxy resin post-cured at 100, 120 and 150°C**

Sample	R-NoPC	R-PC100	R-PC120	R-PC150
<b>Modulus (GPa) according to ISO 527</b>	3.4 ± 0.52	2.7 ± 0.27	2.9 ± 0.06	2.9 ± 0.37
<b>Maximal tensile strength (MPa)</b>	68 ± 8.1	69 ± 5.2	66 ± 3.2	54 ± 3.8
<b>Elongation at break (%)</b>	2.67 ± 0.54	3.56 ± 0.56	3.33 ± 0.04	3.12 ± 0.43

The maximal tensile strength at break does not significantly change for R-PC100 and R-PC120 but decreases by 20% when the post-curing temperature reaches 150°C while the opposite trend was expected [31], [32]. For R-PC150, another phenomenon is altering the mechanical properties. Carbas and al. [33] showed that when the curing temperature is above or near the resin  $T_g$ , the mechanical properties (Modulus and failure tensile strength) of the epoxy resin at room temperature decrease because of a thermal degradation or an oxidative crosslinking (crosslinking within the epoxy polymer).

A slight change of color (from transparent to light yellow) is also evidenced and assigned to an early oxidation of the epoxy resin because the post-curing temperature is approaching the R-PC150 glass transition temperature ( $T_{g,R-PC150} = 165^\circ\text{C}$ , Table 3)[34,35].

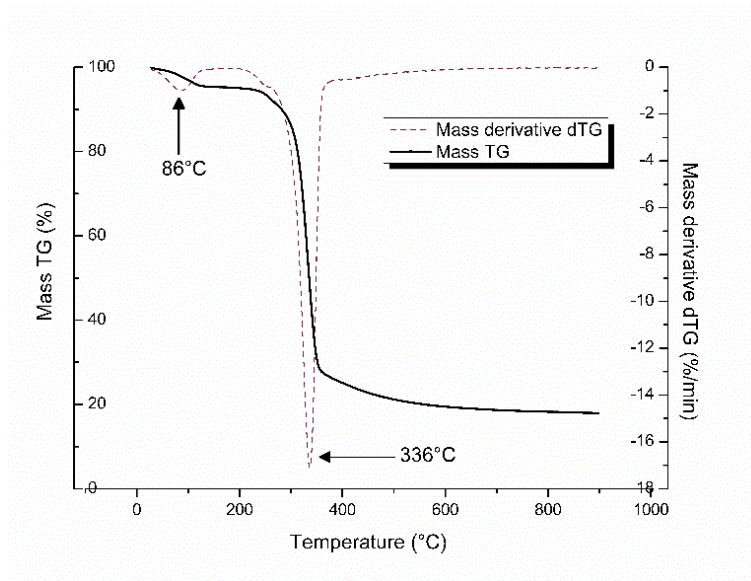
### 3.2.2 Flax fabrics

The second composite component to be studied is the flax fabric used to reinforce the epoxy resin. Flax fibers contain generally between 7 and 10% of moisture in standard conditions (23°C and 50%RH) and this moisture is removed during post-curing at high temperature [9,12,36,37]. TGA tests (Figure 5) show that the present flax fibers contain only 5% of moisture and that this moisture evaporates when the temperature exceeds 86°C. This was the reason for choosing 80°C as curing temperature. During post-curing at 100, 120 or 150°C,

moisture is removed from the fibers and may be extracted from the composites. The higher the temperature is, the more damaging this phenomenon becomes. For instance, when temperature is over 120°C some components of cell walls like waxes are degraded [19].

Tensile tests were carried out onto fabrics by changing the sample length in order to modify the breaking mechanisms. The evolution of the maximal load until breaking for the different samples is shown in Figures 6 and 7. First observations concern the maximal load that decreases when the sample length increases due to a change of the main mode of breaking when longer samples are tested [38–40]. Bledzki and Gassan also showed that the flax fiber tensile strength is dependent on the length of the fiber itself. The longer it is, the more inhomogeneous it will be, weakening its structure [41]. Indeed, for short fibers, a neat breaking is observed at the center of the specimen but when the length of the specimen increases, disentanglement is also noted. Hence the behavior of samples depends on a combination of neat breaking and disentanglement. The latter tends to become predominant for longer specimen. Figure 8 shows the evolution of the maximal load normalized in comparison to raw specimens to see the effect of temperature on the fabrics. It shows that the disentanglement is all the more so retarded by the post-curing temperature when sample length increases because the higher the temperature is, the higher the maximal load will be (compared to other similar length samples).





**Figure 5 – TGA of the Flax Fibers**

Figure 6 and Figure 8 also highlight that for shorter samples (10mm), the higher the temperature of post-curing is, the lower the maximum supported load is, while for longer samples the opposite trend is observed. Indeed, the post-curing process will remove the moisture contained in the fibers. The loss of water will create a modification of the cohesion between the cellulose microfibrils leading to a decrease of the maximal load supported by the fibers [9]. Thus, the maximal load supported will decrease.

Apparent stiffness of fabrics is shown in Figure 9. The apparent stiffness of raw flax fabrics tends to decrease when the specimen length increases. This is due to the occurrence of disentanglement that reduces the global stiffness. The 24 hours curing process at 80°C generates a 10% rise of the fabric apparent stiffness (compare NoPC and raw fabrics) for 10mm samples. Then, the higher the post-curing temperature is, the higher the increase of apparent stiffness will be with a 19% increase for F-PC150. This was expected since heating a single fiber results in an increase of its stiffness because of a reorganization of the fibrils [20]. But, for sample length equal to or higher than 50mm, the impact of post-curing on apparent

stiffness is limited (Fig.6, Fig.9). It seems that disentanglement conceals the impact of the post-curing treatments on fibers.

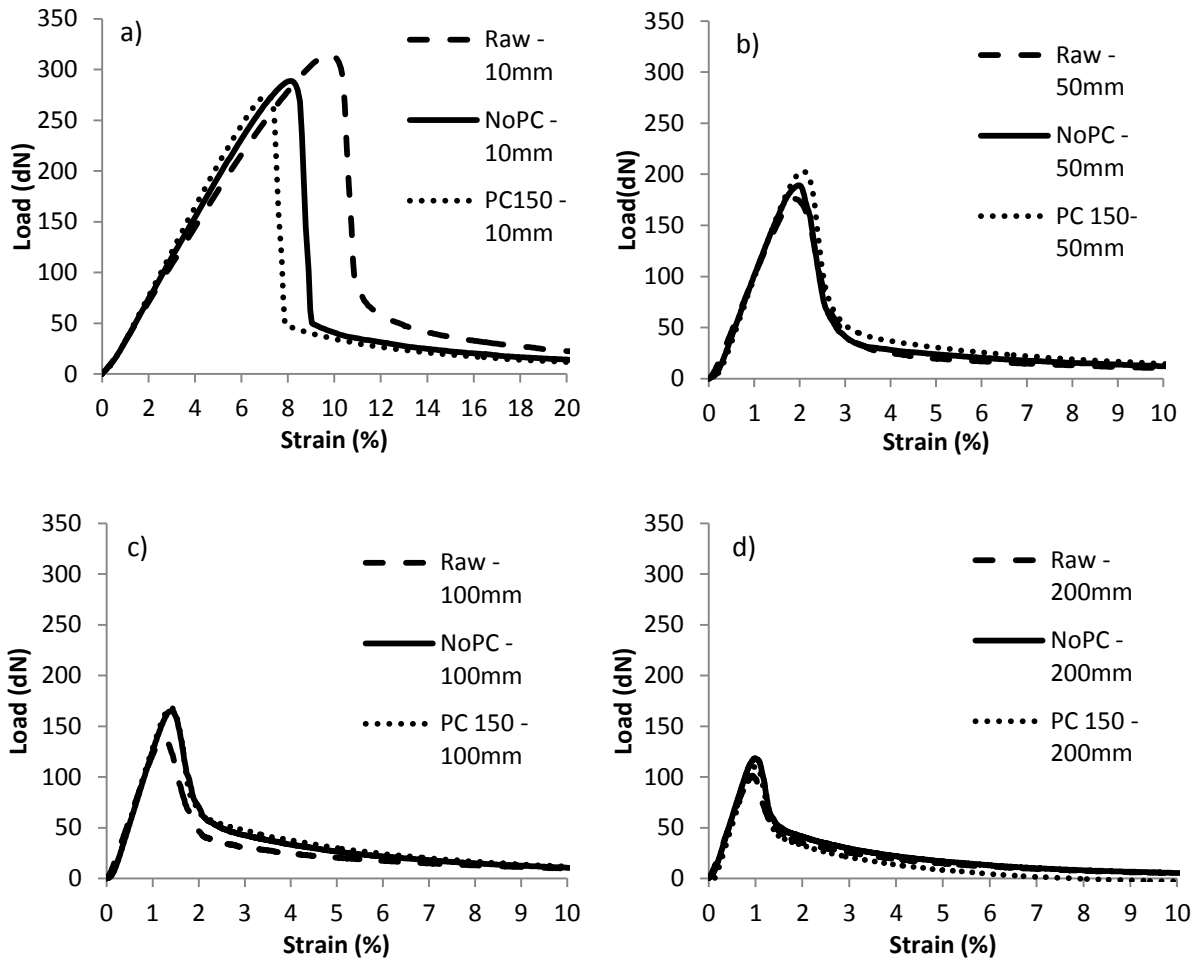
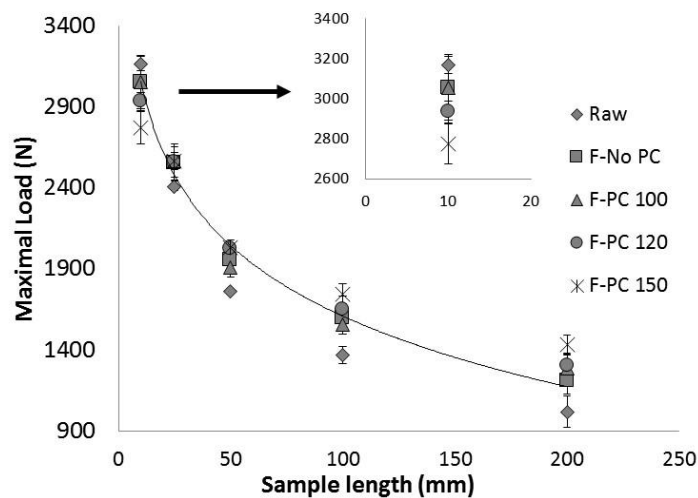
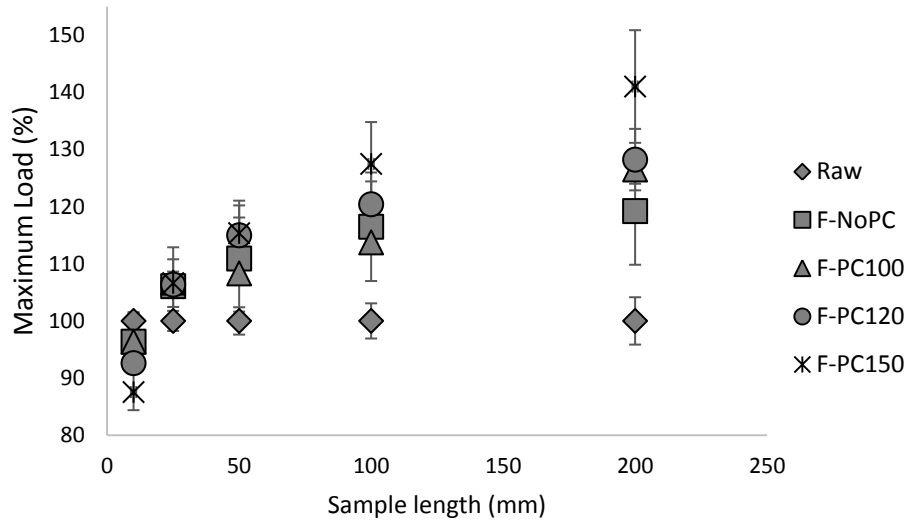


Figure 6 – Load Vs. Displacement of Raw, NoPC and PC150 series for different sample lengths a) 10mm b) 50mm c) 100mm and d) 200mm



**Figure 7 – Evolution of the maximal load (N) Versus Sample length (mm) of the different flax fabric samples**



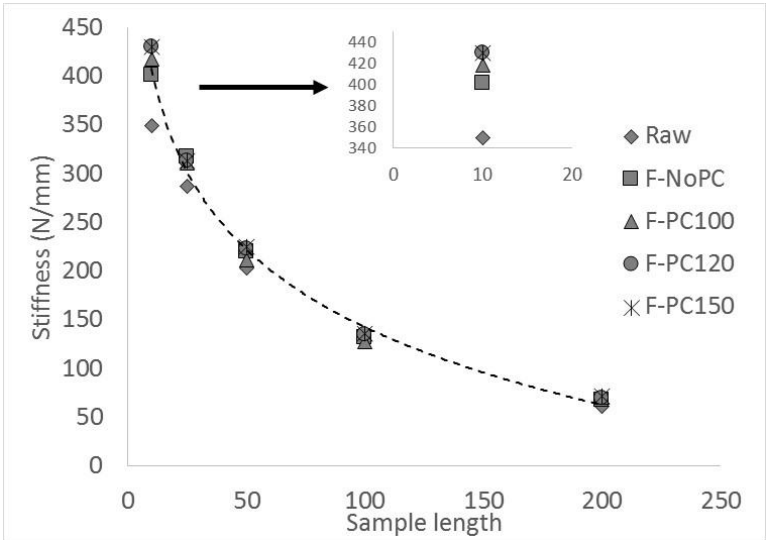
**Figure 8 – Evolution of the normalized maximal load (%) Versus Sample length (mm) for the different flax fabric samples using Raw as reference**

In a composite, only one mode of breaking is encountered (neat breaking) because the resin surrounding fibers drastically reduces the maximal possible strain. For 10mm samples, the increase of the post-curing temperature lowers the maximal loads because the post-curing treatments degrade the fibers or at least lower of the load they can support.

### 3.2.3 Characterization of the interface (SEM+ILSS)

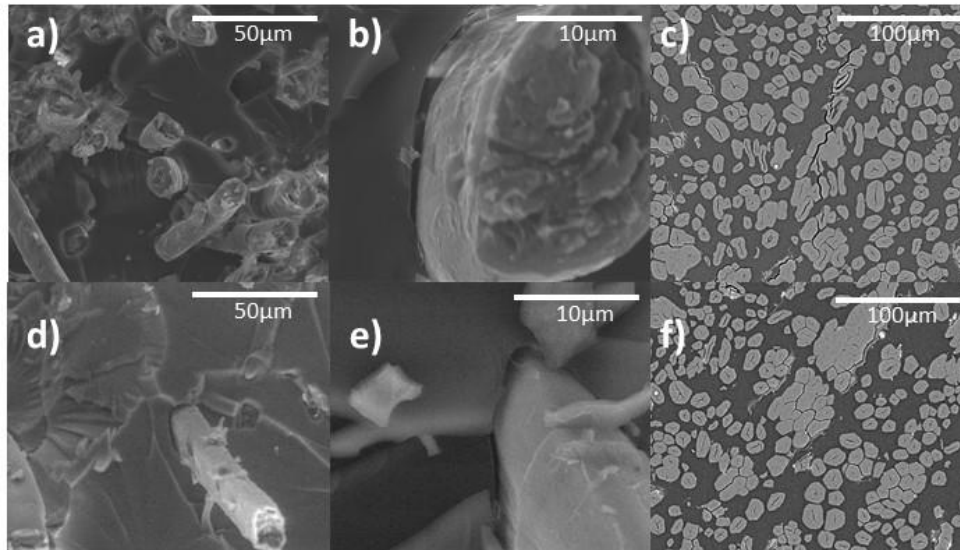
The interfacial zone, where interactions between flax fibers and epoxy resin allow the stress transfer from resin to reinforcement, may also be considered as a specific component of the composite that could be affected by the thermal treatments. Indeed, a modification of the interface between fibers and resin may explain a decrease of the tensile strength of the composite. In order to assess the quality of the interface, ILSS tests and SEM fractographies were carried out. We choose to use ILSS tests in order to determine if there was a modification of the interface quality after the various post-curing treatments. Indeed, ILSS allows to determine on a relative basis the tendencies of the bond strength in a given system

where only the bonding level is changing. Thus, in our case, ILSS may help determining if the interfacial bonding properties could be responsible of the modification of the composite mechanical properties [42]. The ILSS of a composite reinforced with fibers depends on the amount of fibers (synthetic or natural), the processing techniques or even the temperature of measurement. But ultimately, it is mainly dominated by the resin properties and the fiber-matrix interfacial strength [15,43–45]. Synthetic fibers have a rather common geometrical factor whereas natural fibers have a complex geometrical factor (composed of sub-elements) which will improve the fiber-matrix interfacial strength and therefore, have a positive effect on the ILSS values.



**Figure 9 – Stiffness of the different materials Versus Sample length (mm)**

Figure 10 highlights a weak adhesion between fibers and matrix even for NoPC composite. There is no sign that the interface was modified by the post-curing treatment either on the fracture images or on the polished section.



**Figure 10 – a) No PC x1000, b) NoPC x5000, c) NoPC – polished section x800, d) PC150 x1000, e) PC150 x5000, f) PC150 – polished section x800**

In order to confirm the SEM observations by quantitative results, ILSS tests were conducted. Those tests allow to quantify the interfacial interactions and to observe a possible change when the post-curing temperature increases. In this test, the sample undergoes important shear stresses that may cause the failure of the sample. First, it can be observed in Table 5, that the maximal tensile stress in ILSS samples is lower than the tensile strength determined during the tensile tests in Figure 4 with the exception of PC150. Those results allow concluding that the specimens broke under shear stress for NoPC, PC100 and PC120 while no conclusion can be drawn from PC150 results. According to Table 5, it would seem that the post-curing does not affect the composite ILSS whereas the tensile strength decreases significantly.

However, the ILSS for NoPC are 49% higher than those obtain by H. Bos in her study for an epoxy reinforced with flax fabrics composite ( $15.4 \pm 0.4$ MPa) [46] but similar to Meredith's composite (high strength epoxy resin reinforced with flax fabric) that has an ILSS of 23.3MPa [47]. Epoxy composites reinforced with other natural fibers such as jute fibers exhibit an ILSS 53% superior with an ILSS of  $43 \pm 9$  MPa [48]. The same flax fabrics (UD360) impregnated

with an unsaturated polyester resin lead to a composite with a 40% lower ILSS of  $13.73 \pm 0.85$ MPa [49].

**Table 5 – Maximal tensile strength and maximal shear stress for the various composites**

Sample	$\sigma_{max, tensile\ stress}$ (MPa)	Tensile strength (MPa)	ILSS (MPa)
No PC	$205 \pm 15$	252	$23.02 \pm 1.62$
PC 100	$200 \pm 10$	232	$22.48 \pm 1.10$
PC 120	$215 \pm 12$	218	$22.03 \pm 1.30$
PC 150	$195 \pm 11$	136	$>21.8 \pm 1.17$

#### 4. CONCLUSIONS

The objective of this study was to identify the component (fibers, resin or interface) responsible for the progressive change of the composite mechanical properties when a post-curing is carried out at 100, 120 or 150°C. After reproducing the post-curing conditions on each component, static mechanical tests were carried out to assess if an alteration occurred within a 2-hour thermal treatment.

The composite glass transition temperature and the crosslinking rate increase when a post-cure is carried out. The higher the temperature of post-curing, the higher the Tg/crosslinking rate will be (115°C/92% for NoPC and 167°C/100% for PC150). But post-curing leads to a modification of composite mechanical properties, especially at high temperature (150°C). Both tensile strength and elongation at break decrease when the post-curing temperature increases whereas the stabilized modulus does not significantly vary.

Since the interfacial adhesion in NoPC is weak, these alterations cannot be assigned to an interfacial damaging. No significant change of the resin behavior was observed for R-PC100

and R-PC120 but at 150°C, only 15°C below the glass transition temperature, an early oxidation is the first sign of resin damage.

On the contrary, a strong modification of the properties of the fibers when they undergo a thermal treatment similar to post curing was found. Indeed, an increase of the stiffness was highlighted as well as a decrease of the maximal load supported by the fabric when heating at high temperature. However, the impact of heating may be masked by fibers disentanglement when specimen length is high enough. Therefore, tests on short specimens are advised.

It appears that combining a well crosslinked resin with natural fibers to obtain a composite with the highest mechanical properties, is hardly possible. A good compromise for a flax fiber reinforced epoxy composite, would be to perform a 24-hour curing at 80°C followed by a 2 hours post-curing at 120°C. The resulting composite would have a Tg of 145°C and a limited drop of about 14% of the tensile strength compared with an equivalent non-post-cured composite. It would seem that today's epoxy resins are not completely adapted for processing natural fiber reinforced epoxy composites with high (and optimal) mechanical properties. A solution to improve the competitiveness of natural fibers in structural composites would be to associate them with resin that could be cured (rapidly) at low temperature.

## REFERENCES

- [1] Benzarti K, Colin X. Understanding the durability of advanced fibre-reinforced polymer (FRP) composites for structural applications. *Adv. Fibre-Reinforced Polym. Compos. Struct. Appl.*, 2013, p. 361–439. doi:10.1533/9780857098641.3.361.
- [2] Pickering SJ. Recycling technologies for thermoset composite materials—current status. *2nd Int Conf Adv Polym Compos Struct Appl Constr* 2006;37:1206–15. doi:10.1016/j.compositesa.2005.05.030.
- [3] Reynolds N, Pharaoh M. An introduction to composites recycling. In: Goodship V, editor. *Manag. Recycl. Reuse Waste Compos.*, University of Warwick, UK: Elsevier; 2010, p. 3–19. doi:10.1533/9781845697662.1.3.
- [4] Joshi S V., Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Compos Part A Appl Sci Manuf* 2004;35:371–6. doi:10.1016/j.compositesa.2003.09.016.
- [5] Wambua P, Ivens J, Verpoest I. Natural fibres: Can they replace glass in fibre reinforced

- plastics? *Compos Sci Technol* 2003;63:1259–64. doi:10.1016/S0266-3538(03)00096-4.
- [6] Mohanty AK, Misra M, Drzal LT. Sustainable Bio-Composites from renewable resources: Opportunities and challenges in the green materials world. *J Polym Environ* 2002;10:19–26. doi:10.1023/A:1021013921916.
- [7] Haag K, Padovani J, Fita S, Trouvé J-P, Pineau C, Hawkins S, et al. Influence of flax fibre variety and year-to-year variability on composite properties. *Ind Crops Prod* 2017;98:1–9. doi:10.1016/j.indcrop.2016.12.028.
- [8] Charlet K, Baley C, Morvan C, Jernot JP, Gomina M, Bréard J. Characteristics of Hermès flax fibres as a function of their location in the stem and properties of the derived unidirectional composites. *Compos Part A Appl Sci Manuf* 2007;38:1912–21. doi:10.1016/j.compositesa.2007.03.006.
- [9] Baley C, Morvan C, Grohens Y. Influence of the absorbed water on the tensile strength of flax fibers. *Macromol Symp* 2005;222:195–201. doi:10.1002/masy.200550425.
- [10] Alix S, Philippe E, Bessadok A, Lebrun L, Morvan C, Marais S. Effect of chemical treatments on water sorption and mechanical properties of flax fibres. *Bioresour Technol* 2009;100:4742–9. doi:10.1016/j.biortech.2009.04.067.
- [11] Céline A, Fréour S, Jacquemin F, Casari P. The hygroscopic behavior of plant fibers: a review. *Front Chem* 2013;1:43. doi:10.3389/fchem.2013.00043.
- [12] Gassan J, Bledzki AK. Thermal degradation of flax and jute fibers. *J Appl Polym Sci* 2001;82:1417–22. doi:10.1002/app.1979.
- [13] Placet V. Characterization of the thermo-mechanical behaviour of Hemp fibres intended for the manufacturing of high performance composites. *Compos Part A Appl Sci Manuf* 2009;40:1111–8. doi:10.1016/j.compositesa.2009.04.031.
- [14] Cook W, Mehrabi M, Edward G. Ageing and yielding in model epoxy thermosets. *Polymer (Guildf)* 1999;40:1209–18. doi:10.1016/S0032-3861(98)00343-7.
- [15] Kumar DS, Shukla MJ, Mahato KK, Rathore DK, Prusty RK, Ray BC. Effect of post-curing on thermal and mechanical behavior of GFRP composites. *IOP Conf Ser Mater Sci Eng* 2015;75:12012. doi:10.1088/1757-899X/75/1/012012.
- [16] Maseteau B, Michaud F, Irle M, Roy A, Alise G. An evaluation of the effects of moisture content on the modulus of elasticity of a unidirectional flax fiber composite. *Compos Part A Appl Sci Manuf* 2014;60:32–7. doi:10.1016/j.compositesa.2014.01.011.
- [17] Placet V, Cisse O, Boubakar ML. Influence of environmental relative humidity on the tensile and rotational behaviour of hemp fibres. *J Mater Sci* 2012;47:3435–46. doi:10.1007/s10853-011-6191-3.
- [18] Thuault A, Eve S, Blond D, Bréard J, Gomina M. Effects of the hygrothermal environment on the mechanical properties of flax fibres. *J Compos Mater* 2014;48:1699–707. doi:10.1177/0021998313490217.
- [19] Müssig J, Haag K. The use of flax fibres as reinforcements in composites. *Biofiber Reinf. Compos. Mater.*, 2015, p. 35–85. doi:10.1533/9781782421276.1.35.
- [20] Baley C, Le Duigou A, Bourmaud A, Davies P. Influence of drying on the mechanical behaviour of flax fibres and their unidirectional composites. *Compos Part A Appl Sci Manuf* 2012;43:1226–33. doi:10.1016/j.compositesa.2012.03.005.
- [21] Xue Y, Du Y, Elder S, Wang K, Zhang J. Temperature and loading rate effects on tensile properties of kenaf bast fiber bundles and composites. *Compos Part B Eng* 2009;40:189–96. doi:10.1016/j.compositesb.2008.11.009.
- [22] Liang S, Gning PB, Guillaumat L. Quasi-static behaviour and damage assessment of



- flax/epoxy composites. *Mater Des* 2015;67:344–53. doi:10.1016/j.matdes.2014.11.048.
- [23] Bensadoun F, Vallons KAM, Lessard LB, Verpoest I, Van Vuure AW. Fatigue behaviour assessment of flax-epoxy composites. *Compos Part A Appl Sci Manuf* 2016;82:253–66. doi:10.1016/j.compositesa.2015.11.003.
- [24] Berges M, Léger R, Placet V, Person V, Corn S, Gabrion X, et al. Influence of moisture uptake on the static, cyclic and dynamic behaviour of unidirectional flax fibre-reinforced epoxy laminates. *Compos Part A Appl Sci Manuf* 2016;88:165–77. doi:10.1016/j.compositesa.2016.05.029.
- [25] Gillham JK and, Pang KP. Anomalous behavior of Cured Epoxy Resins : Density at room temperature vs. Time and Temperature of cure. Arlington: 1988.
- [26] Enns JB, Gillham JK. Effect of the extent of cure on the modulus, glass transition, water absorptio, and density of an amine-cured epoxy. *J Appl Polym Sci* 1983;28:2831–46. doi:10.1002/app.1983.070280914.
- [27] Fisch W, Hofmann W, Schmid R. Influence of structure and curing conditions on the density, degree of cure, and glass transition temperature during the curing of epoxide resins. *J Appl Polym Sci* 1969;13:295–308. doi:10.1002/app.1969.070130203.
- [28] Acera Fernández J, Le Moigne N, Caro-Bretelle AS, El Hage R, Le Duc A, Lozachmeur M, et al. Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites. *Ind Crops Prod* 2016;85:93–108. doi:10.1016/j.indcrop.2016.02.047.
- [29] Crowson RJ, Arridge RGC. The elastic properties in bulk and shear of a glass bead-reinforced epoxy resin composite. *J Mater Sci* 1977;12:2154–64. doi:10.1007/BF00552236.
- [30] Nicolais L, Landel RF, Giordano-Orsini P. The Glass Transition Temperature of Poly(phenylene oxide): Annealing and Filler Effects. *Polym J* 1975;7:259–63. doi:10.1295/polymj.7.259.
- [31] Aruniit A, Kers J, Krumme A, Poltimäe T, Tall K. Preliminary Study of the Influence of Post Curing Parameters to the Particle Reinforced Composite’s Mechanical and Physical Properties. *Mater Sci* 2012;18:256–61.
- [32] Moussa O, de Castro J, Vassilopoulos a P, Keller T. Long-term physical and mechanical properties of cold curing structural epoxy adhesives. *Proc 6th Int Conf FRP Compos Civ Eng* 2012:1–8.
- [33] Carbas RJC, Marques E a. S, da Silva LFM, Lopes a. M. Effect of Cure Temperature on the Glass Transition Temperature and Mechanical Properties of Epoxy Adhesives. *J Adhes* 2014;90:104–19. doi:10.1080/00218464.2013.779559.
- [34] Tandon GP, Pochiraju K V., Schoeppner GA. Modeling of oxidative development in PMR-15 resin. *Polym Degrad Stab* 2006;91:1861–9. doi:10.1016/j.polyimdeggradstab.2005.11.008.
- [35] Colin X, Marais C, Verdu J. A new method for predicting the thermal oxidation of thermoset matrices: Application to an amine crosslinked epoxy. *Polym Test* 2001;20:795–803. doi:10.1016/S0142-9418(01)00021-6.
- [36] Bourmaud A, Morvan C, Baley C. Importance of fiber preparation to optimize the surface and mechanical properties of unitary flax fiber. *Ind Crops Prod* 2010;32:662–7. doi:10.1016/j.indcrop.2010.08.002.
- [37] Jalaludin Z, Hill C, Curling S. Moisture adsorption isotherms of wood studied using dynamic vapour sorption apparatus. *Int. Res. Gr. Wood Prot., Beijing, China: 2009.*
- [38] Charlet K, Beakou A. Mechanical properties of interfaces within a flax bundle - Part I: Experimental analysis. *Int J Adhes Adhes* 2011;31:875–81. doi:10.1016/j.ijadhadh.2013.01.013.

- [39] Zhu J, Zhu H, Njuguna J, Abhyankar H. Recent development of flax fibres and their reinforced composites based on different polymeric matrices. *Materials (Basel)* 2013;6:5171–98. doi:10.3390/ma6115171.
- [40] Charlet K, Béakou A. Mechanical characterization and modeling of interfacial lamella within a flax bundle. *Procedia Eng* 2011;10:906–11. doi:10.1016/j.proeng.2011.04.149.
- [41] Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. *Prog Polym Sci* 1999;24:221–74. doi:10.1016/S0079-6700(98)00018-5.
- [42] Narkis M, Chen EJH, Pipes RB. Review of methods for characterization of interfacial fiber- matrix interactions. *Polym Compos* 1988;9:245–51. doi:10.1002/pc.750090402.
- [43] Ahmed KS, Vijayarangan S. Tensile, flexural and interlaminar shear properties of woven jute and jute-glass fabric reinforced polyester composites. *J Mater Process Technol* 2008;207:330–5. doi:10.1016/j.jmatprotec.2008.06.038.
- [44] Wu Z, Li J, Huang C, Li L. Effect of matrix modification on interlaminar shear strength of glass fibre reinforced epoxy composites at cryogenic temperature. *Phys Procedia* 2015;67:1068–73. doi:10.1016/j.phpro.2015.06.202.
- [45] Chandrasekaran VCS, Advani SG, Santare MH. Role of processing on interlaminar shear strength enhancement of epoxy/glass fiber/multi-walled carbon nanotube hybrid composites. *Carbon N Y* 2010;48:3692–9. doi:10.1016/j.carbon.2010.06.010.
- [46] Bos HL. The potential of flax fibres as reinforcement for composite materials. Technische Universiteit Eindhoven, 2004. doi:10.6100/IR575360.
- [47] Meredith J, Coles SR, Powe R, Collings E, Cozien-Cazuc S, Weager B, et al. On the static and dynamic properties of flax and Cordenka epoxy composites. *Compos Sci Technol* 2013;80:31–8. doi:10.1016/j.compscitech.2013.03.003.
- [48] Doan TTL, Brodowsky H, Mäder E. Jute fibre/epoxy composites: Surface properties and interfacial adhesion. *Compos Sci Technol* 2012;72:1160–6. doi:10.1016/j.compscitech.2012.03.025.
- [49] Testoni GA. In situ long-term durability analysis of biocomposites in the marine environment. 2015.