

# Thermal and mechanical performances of bamboo strip

Tutea Richmond, Louise Lods, Jany Dandurand, Eric Dantras, Colette Lacabanne, Jean-Michel Durand, Edouard Sherwood, Philippe Ponteins

# ▶ To cite this version:

Tutea Richmond, Louise Lods, Jany Dandurand, Eric Dantras, Colette Lacabanne, et al.. Thermal and mechanical performances of bamboo strip. Materials Research Express, 2021, pp.0. 10.1088/2053-1591/abe060. hal-03138410

# HAL Id: hal-03138410 https://hal.science/hal-03138410

Submitted on 11 Feb 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# **Open Archive Toulouse Archive Ouverte**

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: http://oatao.univ-toulouse.fr/27410

# **Official URL**

DOI : https://doi.org/10.1088/2053-1591/abe060

**To cite this version:** RICHMOND, Tutea and LODS, Louise and DANDURAND, Jany and Dantras, Eric and Lacabanne, Colette and DURAND, Jean-Michel and SHERWOOD, Edouard and Ponteins, Philippe *Thermal and mechanical performances of bamboo strip.* (2021) Materials Research Express. ISSN 2053-1591

# Thermal and mechanical performances of bamboo strip

Tutea Richmond<sup>1</sup>, Louise Lods<sup>1</sup>, Jany Dandurand<sup>1</sup>, Eric Dantras<sup>1</sup>, Colette Lacabanne<sup>1</sup>, Jean-Michel Durand<sup>2</sup>, Edouard Sherwood<sup>2</sup> and Philippe Ponteins<sup>3</sup>

<sup>1</sup> CIRIMAT, Université de Toulouse, Physique des Polymères, 118 Route de Narbonne, 31062 Toulouse Cedex 09, France

<sup>2</sup> Cobratex, 1 Allée Orchidée, Local 8 ZA Activestre, 31390 Carbonne, France

<sup>3</sup> Expleo Group, 13 rue Marie Louise Dissard, 31300 Toulouse, France

E mail: colette.lacabanne@univ tlse3.fr

Keywords: bamboos, strip, mechanical performances, thermal stability

## Abstract

Bamboo strips extracted from Phyllostachys viridiglaucescens, grown in Europe, were analysed to assess their thermal and mechanical properties for composites application. Thermal stability of the European bamboo was studied by Thermogravimetric Analysis (TGA) and compared to the one of species grown in Oceania. An evolution of the chemical composition along the radial direction of the Phyllostachys bamboo was identified by TGA. The inner part of culms shows a higher proportion of hemicelluloses, while the percentage of crystalline cellulose is higher in the outer portion. This evolution of the composition was used to interpret the original data recorded by Dynamic Mechanical Analysis (DMA) of the strips. Glassy tensile modulus founded by DMA increases from the inner part of the culm (6.8 GPa) to the outer part (9.9 GPa). The variation of the cellulose content along the radius of the bamboo culm is related to this increase and shows a good correlation with thermal behaviour. The dynamic relaxations in the shear mode reveal the existence of two secondary relaxation modes sensitive to water. In the order of increasing temperatures, they have been assigned to the mobility of methylol groups and to heterogeneities of the polymeric matrix. By combining Differential Scanning Calorimetry (DSC) and DMA, the response of the viscoelastic transition of bamboo strips, at 210 °C, was evidenced for the first time. Bamboo strips behave as a unidirectional composite reinforced by technical fibres; its particularly high shear glassy modulus (2.3 GPa) deserves to be emphasised.

# 1. Introduction

The depletion of fossil resources is pushing mankind to turn to renewable solutions to produce new organic composites. The use of natural resources has already shown its potential in many areas [1, 2]. The growing interest in materials based on renewable resources, like natural fibres reinforced composites, is reflected in the number of publications over the last few years [3–6]. With more than 1200 known species, bamboo offers a tremendous potential for several reasons: a fast-growing—up to 21 cm per day—and a worldwide availability making it suitable for future industrialisation. Bamboo is endemic in all parts of the world except in Europe [7] where they were first introduced in the middle of the 19th century as ornamental plants. Since 1997, the European Union has been supporting research on bamboo, particularly for ecological applications and energy production [8, 9]. Phyllostachys bamboos, an Asian species grown in Europe, were the most studied species during these framework programs. More recently, Depuydt *et al* investigated the potential of Phyllostachys bamboos for composite applications [10]. They showed that bamboo grown in Europe has fibres with reasonable mechanical properties, and depending on the species, they have a Young's modulus comparable to tropical species. Natural fibres have interesting physical and mechanical properties, combined with a reduced environmental impact, enabling them to respond to societal issues.

Bamboo has a specific heterogeneous structure. The plant presents a hollow culm with an alternation of nodes and internodes. This specific architecture allows the stress distribution caused by external factors along

the culm. Indeed, bamboos can reach up to more than 30 m [11] and thus are subjected to bending forces induced in particular by the wind. The anatomical structure of bamboo internode has been widely described over the years by many researchers [7, 12]. They showed that the transverse cross-section is composed of numerous vascular bundles, which are distributed densely in the outer region of the wall, surrounded by parenchyma tissue. Fibres bundles are composed of a multitude of elementary fibres, embedded into vascular bundles; they play the same role as reinforcing component in composite materials. According to Li *et al* [13], the volume fraction and the mechanical properties of vascular bundles increase linearly from the inner side to the outer side of the culm.

Natural fibres can be considered as composites. They are composed of three main components: cellulose, hemicelluloses and lignin, where cellulose plays the role of reinforcement. Prior studies have already proved the interest of using bamboo fibres as reinforcement in composites. However, in the literature, the mechanical properties of fibres are very different. This is due to several factors as species, position of the fibres in the culm and their chemical composition or extraction processes. The high natural variability of these characteristics makes necessary to characterize the thermal stability and the mechanical behaviour to control the intrinsic heterogeneity of bamboo.

The paper aims to assess the physical properties of bamboo strips. The thermal properties of *Phyllostachys viridiglaucescens* from Europe compared to *Cyrthocloa puser* from Oceania was analysed by ThermoGravimetric Analysis (TGA). The thermal stability of bamboo strips was analysed as a function of the position in the culm. For further investigation of mechanical properties, the variation along the radial direction was studied, thereby enabling to select the best reinforcement for composites. The mechanical performances of Phyllostachys species were checked through static tests and Dynamic Mechanical Analyses (DMA).

## 2. Materials and methods

#### 2.1. Materials

For this research, *Phyllostachys viridiglaucescens* bamboo from Europe was selected and *Cyrthocloa puser* from Oceania was used for comparison. *Phyllostachys viridiglaucescens* and *Cyrthocloa puser* bamboos were supplied by Cobratex. The 3-year-old bamboos were harvested in winter when moisture is expected to be the highest due to colder temperatures which stop the evapotranspiration processes [10]. Samples were provided in tape form with 0.3 mm thick and 5 mm in width. Those were extracted by a purely mechanical process along the longitudinal direction of the culm.

#### 2.2. Methods

#### 2.2.1. ThermoGravimetric analysis

Thermal decomposition of bamboo samples was investigated by TGA. Thermograms were carried out on a TGA Q50 analyser from TA Instruments. Samples were placed in a closed pan with an initial sample amount of 7 to 10 mg. Analyses were done under an oxidizing gas atmosphere (synthetic air) at a heating rate of 10  $^{\circ}$ C min <sup>1</sup> from 30 to 600  $^{\circ}$ C. Three replicates of each TGA thermogram were tested in order to ensure repeatability.

#### 2.2.2. Differential scanning calorimetry

Thermal transitions of bamboo were investigated by Differential Scanning Calorimetry (DSC). Analyses were carried out on DSC7 from Perkin Elmer. Samples with a mass ranging between 10 to 15 mg, were placed in closed aluminium pans. Experiments consist of three heating runs two cooling runs and isothermal annealing at 160 °C from 10 to 120 min. Physical ageing is thus induced in the material. The aim of this protocol is to highlight the glass transition temperature (T<sub>g</sub>) by increasing the ageing overshoot. Measurements were performed between 50 to 250 °C at a constant heating rate of 20 °C min<sup>-1</sup> under a nitrogen flow.

#### 2.2.3. Tensile tests

Tensile tests on single bamboo strip were adapted from the methodology described by Osorio *et al* [14]. This protocol allows us to provide a good gripping of samples and avoids any slippage during tests. To ensure the absence of major damages, bamboo strips were carefully selected. Samples were glued into a frame with a gauge length of 25 mm and conditioned at room relative humidity and room temperature. Tensile tests were performed on a Criterion model 43 electromechanical load frame from MTS System Corporation. Stress-strain curves were gathered with a load cell of 2.5 kN and a crosshead speed of 1 mm min<sup>-1</sup>. Young's modulus was calculated from the slope of the curve in the linear elastic region.



#### 2.2.4. Dynamic mechanical analysis

DMA is a technique used to study and characterise materials. As described by Ward and Sweeney [15], this technique allows us to measure the  $M^*_{\omega_0}(T)$  complex modulus:

$$M_{\omega_0}^*(T) = M_{\omega_0}'(T) + iM_{\omega_0}''(T)$$

with  $M'_{\omega_0}(T)$  and  $M''_{\omega_0}(T)$  are respectively the storage modulus and the loss modulus. The analytical representation for the dynamic mechanical behaviour is based on the Maxwell model and it is described for the isofrequency mode, by the following relationships:

$$M'_{\omega_0}(T) = M_r + (M_g - M_r) \frac{\omega_0^2 \tau(T)^2}{1 + \omega_0^2 \tau(T)^2}$$
$$M''_{\omega_0}(T) = (M_g - M_r) \frac{\omega_0 \tau(T)}{1 + \omega_0^2 \tau(T)^2}$$

where  $M_r$  is the rubbery modulus,  $M_g$  is the glassy modulus,  $\omega_0$  is frequency of strain oscillation and  $\tau$  is the relaxation time. Tensile storage and loss moduli are defined as:  $E'_{\omega_0}$  and  $E''_{\omega_0}$ . Similarly, shear storage and loss moduli are designated as  $G'_{\omega_0}$  and  $G''_{\omega_0}$ .

DMA were performed on the ARES G2 strain-controlled rheometer manufactured by TA Instruments. Samples had the geometry of 50 mm × 5 mm × 0.3 mm strips. Trials were carried out over the temperature range -130 to 210 °C at a heating rate of 3 °C min<sup>-1</sup>. For each sample, two consecutive runs were performed at a fixed frequency of  $\omega_0 = 1$  rad s<sup>-1</sup>, within the linear strain range i.e. 0.1% for the shear mode and 0.03% for the tensile mode. All experiments were replicated three times to check repeatability.

# 3. Results and discussion

#### 3.1. Thermal stability

Thermal stability is one of the most important features during composites processing especially with biosourced materials [16].

#### 3.1.1. Thermal stability of Phyllostachys viridiglaucescens bamboo

Figure 1 presents the TGA thermogram and its Derivative ThermoGravimetry (DTG) thermogram recorded under air atmosphere from *Phyllostachys viridiglaucescens* bamboo.

The temperature of degradation of lignocellulosic materials is governed by the decomposition of their main constituents: hemicelluloses, cellulose and lignin. It was found that the degradation of natural fibres, with a heating rate of 10 °C min<sup>-1</sup>, exhibits a three-step process. The first drop in mass, around 7%, between 25 and 100 °C is associated with moisture release. This value is consistent with previous data published in 2015 by Zakikhani *et al* on four different species of bamboo, showing that the moisture rate was between 5 and 11% [17].

After the evaporation of water, there is no significant event till 200 °C. Thermal degradation starts at 200 °C, with a rapid mass loss linked to the decomposition of volatile matter from bamboo. The DTG curves display a shoulder peak at 284 °C: it is mainly due to the decomposition of hemicelluloses, the least thermally stable components [17, 18]. Several authors attribute this thermal behaviour to its amorphous structure and low molecular weight [17, 19]. It is consistent with the behaviour of xylan, a representative molecule for



hemicelluloses that starts to decompose between 190 °C–220 °C with a maximum decomposition around 260 °C and 270 °C [18, 19].

At higher temperatures, another peak is observed with a maximum loss rate at 316 °C. This degradation is mainly attributed to cellulose [17]. In contrast with hemicelluloses, cellulose has a semi-crystalline microstructure with a high molecular weight explaining its better thermal stability. Note that the degradation of pure cellulose occurs between 315 °C–400 °C with a maximum mass loss rate at 355 °C [19].

The lignin decomposition is well-defined in air atmosphere at 471 °C. However, this peak is not only explained by the combustion of remaining lignin but also by the combustion of char (i.e. residual carbon compounds) [18, 20]. Among the three main components of natural fibres, lignin is the most difficult compound to decompose. Pure lignin degradation occurs slowly on a wide temperature range from 210 to 900 °C [18]. This thermal behaviour is mainly associated with its complex three-dimensional network composed of three kinds of benzene-propane units randomly cross-linked [19].

These initial results show that the choice of the polymer matrix where bamboo reinforcement will be introduced is important; in other words, natural reinforcement limits the processing temperature of composites.

#### 3.1.2. Comparison of European bamboo and Oceanian bamboos

Experiments were carried out on bamboo reinforcements grown and harvested at two different locations, to highlight its possible influence on the thermal stability. Figure 2 presents TGA curves of European bamboo and Oceanian bamboo under oxidizing environment.

Some qualitative observations can be made from figure 2. Both samples have the same combustion behaviour with three clear mass losses as previously described. Water desorption of both samples is at the same order of magnitude; it varies between 6% and 10%. In addition, we have found that the mass loss for bamboos occurs over a narrow temperature range. *Phyllostachys viridiglaucescens* and *Cyrthocloa puser* have practically the same thermal stability as it can be deduced from chemical composition [18] and in particular from hemicelluloses content [21, 22].

Additional interpretations could be made, with supplementary parameters such as the age of the bamboo or the location within the culm of the extracted strips. Since one of the characteristics of natural materials is the variability with respect to properties, it is important to check this variability in order to control of the performances of the various strips.

#### 3.1.3. Influence of position of strips along the culm

TGA analyses were performed on European bamboo in order to compare the thermal stability of bamboo strips extracted along the culm. The studied strips were extracted from three different bamboo culms (labelled as: 1,2,3) at three different heights: Bottom (B), Middle (M) and Top (T). Figures 3(a) and (b) show respectively the comparison of the TGA curves obtained at a given height for three different culms and the comparison of the TGA curves obtained for the same culm at different heights.

First, for a given height, the thermal behaviour of a bamboo to another is similar. The same trend is visible for strips extracted in individual culms. As seen earlier, strips degradation consists of three steps. For the first step, the evaporation of water is independent of the culm and the level on a given culm. These values, reported in table 1, range approximately between 8.5% for a middle section to 10% for a bottom section. Zakikhani *et al* 



	Position	Water loss (%)	T <sub>ONSET</sub> (°C)
Bamboo 1	В	10	241
	М	09	236
	Т	10	235
Bamboo 2	В	10	249
	М	09	250
	Т	09	248
Bamboo 3	В	09	245
	М	08	248
	Т	09	249

exhibit different results and observe a clear distinction of the moisture amount for the same culm, with results that vary by up to 6% [17].

The second mass loss is due to the combustion of the volatile matter as cellulose, hemicelluloses and partial decomposition of lignin. From figure 3(a), it is clear that the thermal stability of bamboo 1 is significantly different from the two others. Indeed, as shown in table 1, the first onset degradation of the latter, over the three studied levels, occurs at lower temperatures. This difference in stability is more noticeable on bamboo samples taken at mid-height and at the top. This observation is explained by a different composition between the samples. By studying the thermal stability of fibres from poplar, Wang *et al*, attributed this shift to the



hemicelluloses content variation [22]. Upon decrease of hemicelluloses content, the onset temperature, corresponding to the thermal stability, increases. Furthermore, on the third mass loss, the strips from bamboo 1 also show a singular behaviour. The mass loss, especially for the samples from the middle and the bottom of the culm is sharp. As explained above, the events in this temperature range are mainly driven by the degradation of residual lignin and oxidation of char. This sudden mass loss may be related to the chemical structure of the lignin which is complex due to its three-dimensional network. On the other hand, in figure 3(b), samples from the same culm have almost identical thermal stability, with the first onset degradation that occurs in a reduced temperature range. There is no influence of the height position of the extracted strips and their thermal stability for a single culm.

The thermal stability of bamboo strips is partly controlled by their chemical composition. Considering the heterogeneity of the plant cell wall, it is necessary to carry out extensive characterization of the thermal properties within the thickness of the culm.

Figure 4 shows the TGA and DTG curves, under oxygen environment, of bamboo strips taken from the inner, middle and outer parts of the culm. The mass loss thermograms of the three samples show the same degradation behaviour with three events over the temperature range. The moisture content of the three samples is about 8%. The mass loss between 150 °C and 350 °C, clearly suggests that it occurs in two steps. The DTG curves highlight these two events. Between 200 °C and 300 °C, the presence of a shoulder points out the decomposition of hemicelluloses. This shoulder has an increasing amplitude from the external to the internal part of the culm. This would suggest a higher amount of hemicelluloses in the inner part of the bamboo. Between 300 °C and 350 °C the cellulose decomposes [17]. On the DTG profiles, the peaks mainly attributed to cellulose degradation show a maximum decomposition rate at 320 °C. The amorphous component degrades first, then the shoulder reveals the degradation of the crystalline component. Note that the magnitude of this shoulder is decreasing from the outer part to the inner part of the culm. Recent data from Hu *et al* are consistent with the fact that a higher amount of crystalline cellulose is located at the periphery of the culm [23]. Accordingly, a higher concentration of technical fibres is located at the periphery of the culm which confirms the previous finding [13].

The final mass loss resulting from the degradation of the residual lignin and the oxidation of char compounds takes place at higher temperatures. On the DTG curve of the external strips, the peak associated with this phenomenon is shifted to lower temperatures. This suggests that the external strip lignin has a different chemical structure with a lower thermal stability.

TGA analyses performed for this paper used to evaluate the thermal properties of the natural reinforcements, it seems also a good way to estimate their intrinsic composition [24]. In this work, experiments have shown that the thermal stability of bamboo strips for a given culm does not vary from bottom to the top. But it varies significantly along the radial direction, with greater thermal stability for the external strips. Accordingly, further investigations will be made on strips extracted from the outer of the culm.

#### 3.2. Thermal transitions

The analysis of transitions in bamboo strips was performed by DSC. Thermograms were recorded over the temperature range corresponding to the thermal stability range of the strips as defined by the onset temperature of TGA curves. Two scans were performed for each sample. DSC curves of the first-run show, between 0 °C and 150 °C, an endothermic phenomenon associated with water desorption according to the literature on bamboo [17] but also in other natural fibres like jute [25–27]. Above 150 °C, there are no exothermic or endothermic



events. Some researchers have extended the trials by analysing the calorimetric response of natural fibres at higher temperatures up to more than 400 °C. In that temperature region, DSC curves display endothermic and exothermic events due to thermal degradation of the various constituents of such fibres [25–27].

After an initial scan, isothermal physical ageing was carried out, with different isothermal times ranging from 10 to 120 min.

Figure 5 presents the DSC curves obtained after physical ageing at 160 °C. Upon ageing, an endothermic event was revealed at around 180 °C. This overshoot of heat capacity, shifts to higher temperatures with increasing ageing time, which is typical of physical ageing induced in amorphous regions of polymers. Physical ageing in synthetic polymers has been widely studied and occurs at temperatures close to the glass transition. It leads to the formation of additional physical bonds in the amorphous phase. The disruption of such interactions is observed as an endothermic overshoot in the range of the glass transition. In bamboo strips, the step of the glass transition cannot be observed; then the overshoot revealed upon ageing indicates the range of the glass transition. The shift indicates an evolution of the glass transition upon annealing. Note that few data are available in the literature on the calorimetric response of natural materials. Martin *et al* investigated sisal fibres and their constituents by DSC analysis but without any physical ageing [28]. The DSC curves of the constituents isolated from raw fibres do not show any thermal event at 180 °C.

#### 3.3. Young's modulus and tensile strength

The mechanical properties of bio sourced composites often show a high variability depending on several factors as species, method of extraction, location of the extracted material...Because of its specific architecture, bamboo is highly anisotropic and heterogeneous. Its mechanical properties gradually increase from the inner part of the culm to the outer part [13]. Thus, tensile tests are only performed on external strips, which are also more thermally stable as seen previously.

A typical tensile stress-strain curve for the bamboo strip is presented in figure 6. Trials were conducted on 94 specimens from different culms. At room temperature, bamboo has a brittle fracture with a strain to failure up to 2%. The tensile strength of  $210 \pm 44$  MPa is analogous with values reported for epoxy/bamboo fibres composites [29]. The Young's modulus of the strips was calculated from the linear region of the stress-strain curves: the recorded value is  $10.0 \pm 2.4$  GPa.

It is interesting to compare this value with Young's modulus measured by Lods *et al* of 26 GPa [30] on *Phyllostachys viridiglaucescens* technical fibres. Considering that technical fibres play the role of reinforcement in the strips, it is consistent to find a value of strip modulus of 38% of elementary fibres.

Recent data of the tensile modulus of bamboo culms report values between 18 to 28 MPa [31]. The tensile modulus of bamboo culm is dependent upon several factors: the heterogeneous distribution of the fibres through the wall thickness [13, 32] and the percentage of parenchyma tissue which has a lower tensile modulus than the fibres [33]. This last point explains the relatively low modulus of bamboo culm regarding bamboo strips. By conducting tensile tests on Italian bamboo culms, Fabiani observed that the failure of some specimens occurs first in the inner part of the culm due to the lower density of fibres [34]. In their research, Osorio *et al* have seen the same trend: the mechanical properties of an elementary fibre of bamboo are higher to those of a technical fibre (+16.3%), which are superior to those of bamboo culm (+168.8%) [12].





### 3.4. Dynamic mechanical relaxation

#### 3.4.1. Dynamic mechanical analyses in shear mode

Figure 7 presents the DMA thermograms for bamboo strip in shear mode, in the temperature range from -150 °C to 220 °C. Two consecutive runs were performed; the first one represents the hydrated state of the material and the second one the dehydrated state. DMA curves obtained from bamboo strips show similar trends compared to synthetic polymers. But the dynamic mechanical behaviour of this natural composite is more complex to investigate due to the various levels of organisation of the natural matrix.

The G'loss modulus thermograms show three distinct relaxation modes:

- Two secondary relaxations at lower temperature, respectively located between -130 and  $-50\ ^\circ C$  and between  $0\ ^\circ C$  and  $100\ ^\circ C$
- One primary relaxation starting at 150 °C

#### 3.4.1.1. Secondary relaxations

The secondary relaxations are associated with localised molecular mobility. They are more intense for the hydrated state. This observation suggests interactions of mobile species with water molecules. As far as we know, there are no data in the literature on DMA of bamboo strip in this temperature range. Analogous modes were observed in the same temperature range in wood. They have been attributed to the mobility of methyl groups coupled to water molecules in the amorphous regions [35]. This last observation is confirmed by the fact that, on the second run, this relaxation is shifted to higher temperatures with a smaller amplitude pointing out a moisture dependency. Sun *et al* [36] conducted DMA on dry wood and observed a broad peak relaxation at -50 °C with a shoulder around -120 °C which were attributed respectively to the mobility of absorbed water and methylol groups. But their second run only exhibits a peak due to the mobility of methylol groups around -105 °C. Obviously, a macroscopic wood sample cannot be directly compared to natural fibres, but the relaxations

involve similar entities. The above findings confirm the assignment of relaxation modes recorded in bamboo strip. The peak observed on the first scan corresponds to the mobility of water molecules in interaction with methylol groups. On the second scan, the sample is in a dehydrated state. We have assigned the peak at -50 °C to the intrinsic localised mobility of methylol groups.

Note that significant changes on DMA thermograms of bamboo strips occur above 0 °C. The first scan exhibits a broad peak between 0 °C and 100 °C. On the second scan, it decreases in magnitude and it is shifted towards higher temperatures. It has been associated with heterogeneities due to the removal of water molecules. DMA analyses performed on bamboo strips in flexural bending mode, by Das and Debrata [37] show a loss modulus peak between 50 and 150 °C. This relaxation is still observed even after different alkaline treatments which have the effect of removing hemicelluloses. It sounds to have the same origin than the secondary mode we observed in this work.

#### 3.4.1.2. Primary relaxation

At higher temperature, around 210 °C, another phenomenon is observed in bamboo strips on both runs; the intensity of this peak suggests that we are dealing with the viscoelastic relaxation i.e. the mechanical manifestation of the glass transition designated as the  $\alpha$  relaxation. This assignment is confirmed by the DSC observation after ageing of an overshoot that is characteristic of the glass transition around 180 °C. This phenomenon is due to the delocalised molecular mobility in the amorphous regions of the cell wall matrix. To our knowledge, it is the first observation of the viscoelastic shear relaxation for bamboo strips.

It is interesting to compare this mode with the viscoelastic relaxation observed in wood [35, 36]. This relaxation was associated with the micro-Brownian mobility in the non-crystalline region of constitutive polymers of the cell wall.

As shown in figure 7, the G' storage modulus of bamboo strips exhibits a very large glassy plateau up to 170 °C. At room temperature, the shear storage modulus is 2.1 and 2.3 GPa for the hydrated and dehydrated state, respectively. From the comparison of the first and second scan, it is evident that water is implied in the secondary relaxations. Accordingly, the glassy plateau of dehydrated strips is more stable over the same temperature range. These values are particularly high in comparison with synthetic organic polymers.

#### 3.4.2. Dynamic mechanical analyses in elongation mode

DMA were also performed in the elongation mode on bamboo strips extracted from the outer part of the culm. The storage modulus shows a similar behaviour than the shear mode. Indeed, the glassy plateau is large and stable over the studied temperature range indicating a good thermomechanical stability of bamboo strips. At 200 °C, a drop of the modulus is observed due to the viscoelasticity as previously observed for the shear mode in figure 7. At room temperature, the storage modulus E' of the outer strips is 9.9 GPa. These values are consistent with the results of the tensile tests previously exposed in 3.3. Note that the order of magnitude of E' for bamboo strip is much higher than the one recorded for bamboo culm (less than 20 kPa) by Huang *et al* [38]. This lag may be explained by the increase of the volume fraction of the vascular bundles [13, 32], and thus of the number of the technical fibres along the bamboo thickness. Hence, it is evident that the mechanical properties gradually increased from the inner strips of *Phyllostachys viridiglaucescens* bamboo, which show values around 6.8 GPa. As the results obtained in TGA, mechanical properties show a high dependence on the chemical composition, the greater amount of fibres in the outer part of the culm, and thus of cellulose, leads to better mechanical properties [10].

It is interesting to note that previous data on bamboo strips are consistent with the compilation of our TGA data and DMA findings showing that the elongation modulus is governed by the density of fibres.

## 4. Conclusions

This study, conducted on bamboo strips grown and harvested in Europe, allowed the determination of their thermomechanical properties useful for future composite applications.

The thermal stability of bamboo is a key factor for composite processing. It was determined until 200 °C and only shows minor dependence upon species and native regions. The homogeneity within a culm was studied in Phyllostachys viridiglaucescens. The analysis of TGA thermograms exhibits that the thermal stability of bamboo strips varies with their position along the culm radius that has been attributed to the evolution of its chemical composition. The greater percentage of hemicelluloses in the inner region and more crystalline cellulose in the outer region mainly explains this behaviour. However, for a given culm, based on the experiments performed, there are no significant differences in thermal stability from the bottom to the top of the bamboo culm.

This study has shown that the dynamic mechanical properties, in the elongation mode, of bamboo follow the same trend as thermal properties, with a higher glassy modulus at the periphery of the culm (9.9 GPa) than in the inner part (6.8 GPa). This variation is directly linked to the cellulose content: the higher the percentage of cellulose is, the higher the performance of the strip is. The value of glassy tensile modulus of 9.9 GPa from strips extracted from the outer part agrees with the value of their Young modulus (10.0  $\pm$  2.4 GPa) determined by tensile tests.

The analysis of the shear loss modulus in DMA provides complementary data. Two secondary relaxation modes sensitive to water were evidenced and attributed respectively to the mobility of methylol groups and heterogeneities of the polymeric matrix, in the order of increasing temperature. At higher temperature, this mode highlights the presence of a viscoelastic transition at 210 °C, i.e. the mechanical manifestation of the glass transition. This relaxation mode was attributed to delocalised molecular mobility in the amorphous region of the cell wall matrix. A typical physical ageing event observed by DSC, with an overshoot shifted towards higher temperatures when the ageing time increases, confirms the assignment of the mode at 210 °C to the viscoelastic relaxation.

### Acknowledgments

This work was carried out within the framework of the BAmboo long fibre reinforced biobased Matrix COmposites (BAMCO) program supported by BPI and the Conseil Régional d'Occitanie.

## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

#### **ORCID** iDs

Colette Lacabanne https://orcid.org/0000-0003-3286-9707

# References

- [1] Faruk O and Sain M 2015 Biofiber Reinforcements in Composite Materials (Amsterdam: Elsevier/WP, Woodhead Publ)
- [2] Joshi S V, Drzal L T, Mohanty A K and Arora S 2004 Are natural fiber composites environmentally superior to glass fiber reinforced composites? Composites Part A: Applied Science and Manufacturing 35 371 6
- [3] Dunne R, Desai D, Sadiku R and Jayaramudu J 2016 A review of natural fibres, their sustainability and automotive applications J. Reinf. Plast. Compos. 35 1041 50
- [4] Kanaginahal G M, Hebbar H S and Kulkarni S M 2019 Influence of weave pattern and composite thickness on mechanical properties of bamboo/epoxy composites Mater. Res. Express 6 125334
- [5] Pickering K L, Efendy M G A and Le T M 2016 A review of recent developments in natural fibre composites and their mechanical performance Composites Part A: Applied Science and Manufacturing 83 98 112
- [6] Scherer J F and Bom R P 2018 Determination of shear modulus in bamboo fibers composite in torsion tests Mater. Res. Express 6 035310
- [7] Liese W 1987 Research on bamboo Wood Sci. Technol. 21 189 209
- [8] Gielis J 2000 Future possibilities for bamboo in European agriculture
- [9] Hunter I 2003 Bamboo resources, uses and trade: the future? Journal of Bamboo and Rattan 2 319 26
- [10] Depuydt D E C, Billington L, Fuentes C, Sweygers N, Dupont C, Appels L, Ivens J and van Vuure A W 2019 European bamboo fibres for composites applications, study on the seasonal influence Ind. Crops Prod. 133 304 16
- [11] Liese W and Köhl M 2015 Bamboo: The Plant and its Uses (Cham Heidelberg New York NY Dordrecht London: Springer)
- [12] Osorio L, Trujillo E, Lens F, Ivens J, Verpoest I and Van Vuure A 2018 In depth study of the microstructure of bamboo fibres and their relation to the mechanical properties J. Reinf. Plast. Compos. 37 1099 113
- [13] LiH and Shen S 2011 The mechanical properties of bamboo and vascular bundles J. Mater. Res. 26 2749 56
- [14] Osorio L, Trujillo E, Van Vuure A W and Verpoest I 2011 Morphological aspects and mechanical properties of single bamboo fibers and flexural characterization of bamboo/epoxy composites J. Reinf. Plast. Compos. 30 396 408
- [15] Ward I M and Sweeney J 2013 Mechanical Properties of Solid Polymers (Chichester, West Sussex, United Kingdom: Wiley)
- [16] Ochi S, Takagi H and Niki R 2002 Mechanical properties of heat treated natural fibers J. Soc. Mater. Sci. Japan 51 1164 8
- [17] Zakikhani P, Zahari R, Hameed Sultan M T and Abang Abdul Majid D L 2015 Thermal degradation of four bamboo species Bio. Resources 11 414 25
- [18] Cao W, Li J, Martí Rosselló T and Zhang X 2019 Experimental study on the ignition characteristics of cellulose, hemicellulose, lignin and their mixtures J. Energy Inst. 92 1303 12
- [19] Yang H, Yan R, Chen H, Lee D H and Zheng C 2007 Characteristics of hemicellulose, cellulose and lignin pyrolysis *Fuel* 86 1781
   [20] Lu J Jand Chen W H 2015 Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by
- thermogravimetric analysis Appl. Energy 160 49 57
- [21] Reddy K O, Maheswari C U, Reddy D J P and Rajulu A V 2009 Thermal properties of Napier grass fibers Mater. Lett. 63 2390 2
- [22] Wang Q, Xiao S and Q Shi S 2019 The effect of hemicellulose content on mechanical strenght, thermal stability, and water resistance of cellulose rich fiber material from poplar *Bio. Resources* 14 5288 300

- [23] Hu M, Wang C, Lu C, Anuar N I S, Yousfani S H S, Jing M, Chen Z, Zakaria S and Zuo H 2020 Investigation on the classified extraction of the bamboo fiber and its properties J. Nat. Fibers 17 1798 808
- [24] Carrier M, Loppinet Serani A, Denux D, Lasnier J M, Ham Pichavant F, Cansell F and Aymonier C 2011 Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass *Biomass Bioenergy* 35 298 307
- [25] Kabir M, Islam M N and Wang H 2013 Mechanical and thermal properties of jute fibre reinforced composites Journal of Multifunctional Composites 171 6
- [26] Pandey S N, Day A and Mathew M D 1993 Thermal analysis of chemically treated jute fibers Textile Res. J. 63 143 50
- [27] Ray D, Sarkar B K, Basak R K and Rana A K 2002 Study of the thermal behavior of alkali treated jute fibers J. Appl. Polym. Sci. 85 2594 9
   [28] Martin A R, Martins M A, da Silva O R R F and Mattoso L H C 2010 Studies on the thermal properties of sisal fiber and its constituents
- Thermochim. Acta 506 14 9
  [29] Huang J K and Young W B 2019 The mechanical, hygral, and interfacial strength of continuous bamboo fiber reinforced epoxy composites *Composites Part B: Engineering* 166 272 83
- [30] Lods L, Richmond T, Dandurand J, Dantras E, Lacabanne C, Durand J M, Sherwood E, Hochstetter G and Ponteins P 2020 Thermal stability and mechanical behavior of technical bamboo fibers/bio based polyamide composites *J. Therm. Anal Calorim.* (in press) (https://doi.org/https://doi.org/10.1007/s10973 020 10445 z)
- [31] Javadian A, Smith I F C, Saeidi N and Hebel D E 2019 Mechanical properties of bamboo through measurement of culm physical properties for composite fabrication of structural concrete reinforcement *Front. Mater.* 6 15
- [32] Chen H, Cheng H, Wang G, Yu Z and Shi S Q 2015 Tensile properties of bamboo in different sizes J. Wood Sci. 61 552 61
- [33] Shao Z P, Fang C H, Huang S X and Tian G L 2010 Tensile properties of Moso bamboo (Phyllostachys pubescens) and its components with respect to its fiber reinforced composite structure Wood Sci. Technol. 44 655 66
- [34] Fabiani M 2015 Physical and mechanical properties of Italian bamboo culms X World Bamboo Congress (South Korea)
- [35] Zhang T, Bai S L, Zhang Y F and Thibaut B 2012 Viscoelastic properties of wood materials characterized by nanoindentation experiments Wood Sci. Technol. 46 1003 16
- [36] Sun N, Das S and Frazier C E 2007 Dynamic mechanical analysis of dry wood: linear viscoelastic response region and effects of minor moisture changes Holzforschung 61 28 33
- [37] Das M and Chakraborty D 2006 Influence of mercerization on the dynamic mechanical properties of bamboo, a natural lignocellulosic composite Ind. Eng. Chem. Res. 45 6489 92
- [38] Huang S, Jiang Q, Yu B, Nie Y, Ma Z and Ma L 2019 Combined chemical modification of bamboo material prepared using vinyl acetate and methyl methacrylate: dimensional stability, chemical structure, and dynamic mechanical properties *Polymers* 11 1651