Study Of A Coupled Mechanical-Hygrothermal Degradation Of Bio-Based Composites

Arnaud Regazzi, Stéphane Corn, Patrick Ienny, Anne Bergeret, Jean-Charles Benezet

To cite this version:

Arnaud Regazzi, Stéphane Corn, Patrick Ienny, Anne Bergeret, Jean-Charles Benezet. Study Of A Coupled Mechanical-Hygrothermal Degradation Of Bio-Based Composites. DURACOSYS 2012, Sep 2012, Bruxelles, Belgium. hal-03233776

HAL Id: hal-03233776
https://hal.mines-ales.fr/hal-03233776

Submitted on 25 May 2021

Study Of A Coupled Mechanical-Hygrothermal Degradation Of Bio-Based Composites

Regazzi A.[1], Corn S.[1], Ienny P.[1], Bergeret A.[1], Bénézet J.C.[1]

[1] École des Mines d'Alès, Centre CMGD, 6 avenue de Clavières, F-30319 ALES CEDEX

ABSTRACT

This work deals with the characterization under environmental conditions of the behavior of polylactic acid/flax composites. In order to simulate real-life aging conditions, the influence of three different kinds of damage (hydric, thermal and mechanical) was assessed.

Materials were immersed in water and they were characterized thanks to different techniques such as weight and dimension measurements as well as analysis of the natural mode of vibration. Results show the strong influence of both temperature and fiber content in the polymer regarding water absorption and evolution of mechanical properties. Water uptake induces swelling and plasticization of the composite which results in a decrease of the dynamic elastic modulus and an increase of the damping factor. Irreversible damage of the materials may occur for long aging times and lead to an increase of dynamic elastic modulus.

The long-term behavior of these materials was evaluated by creep tests. They show a decrease of the elastic modulus even without a degrading environment. Nevertheless, in conditions suitable for aging, the modulus drops drastically.

1. INTRODUCTION

1.1. Context

Current sustainable development policy has resulted in a growing demand for bio-based materials. In the field of composites, a wide range of polymers combined with numerous natural fibers allow to meet various criteria in terms of physical properties. This study focuses on the combination of polylactic acid and flax fibers because of their low price, their excellent mechanical properties and their biodegradability. Several papers underline some interesting properties of such composites: [1], [2], [3]. Consequently, this material and other bio-based composites are likely to increase their market share. Unfortunately technical difficulties curb a massive use of these composite [4]. Among them, cultivation of fibers, manufacture of composite and knowledge of their behavior are the most important. Their natural origin may cause significant modification of their behavior when they are exposed to environmental conditions (i.e. in the prospect of outdoor applications). Indeed, using such materials in real life conditions leads to specific problems of aging due to different kinds of factors like water, temperature, mechanical loadings and sun. On the one hand temperature and humidity hold sway over mechanical properties of vegetal fibers, and on the other hand the polylactic acid is considered as a biodegradable polymer partly because of its low glass transition temperature. Consequently it makes these composites even more sensitive to environmental conditions and the understanding of their behavior even more complicated.

Literature shows that various physico-chemical processes may take place into these composites like plasticization, swelling, hydrolysis, interfacial decohesion [5]… They generally lead to the deterioration of their mechanical behavior bust most important they are inextricably interdependent. The presence of repeated mechanical loadings inherent to the use of such materials as structural parts may accelerate aging mechanisms or even induce others [6]. Anyway, the prediction of the mechanical properties in given conditions remains poorly known and in main cases, environmental and mechanical aging are studied separately. That is why it is suggested in this study to assess the effects of their combination.

1.2. Methodology

Firstly, the approach consists in studying the influence of the sole hygrothermal aging of the material by evaluating the evolution of its viscoelastic behavior. These properties are determined thanks to an unusual, but quick and non-destructive method which involves the monitoring of free natural vibrations of material samples by using a laser sensor.

Secondly, the influence of mechanical loadings in a non-aging environment is assessed. Tensile creep is intended to evaluate long-term behavior of materials.

The final step focuses on the in situ analysis of the coupling of mechanical solicitations and hygrothermal aging. Samples are exposed to a hygrothermal environment while they are subjected to a mechanical loading. In this case, the material is supposed to show an evolution of its mechanical properties which is different from the basic addition of the effects of mechanical and hygrothermal aging taken separately. Consequently, the combination of successive and in situ characterizations allows the influence of the coupling component to be quantified within the global degradation mechanism.

2. MATERIALS AND METHODS

2.1. Materials

The purpose of this paper is to provide possible answers to these inter-related questions by studying the mechanical behavior of PLA (polylactic acid) / flax fiber biocomposites with various fiber weight contents:

- 0% (neat PLA) hereafter named PLA
- 20% hereafter named PLA-L20
- 30% hereafter named PLA-L30

The PLA 7000D resin was obtained from NatureWorks® company and is designed for injection stretch blow molded applications. This grade of PLA has a density of 1.24 g/cm³, a glass transition temperature between 55 and 60°C and a melt temperature between 155 and 165°C [7].

The short flax fibers (Linum usitatissimum) used for this study were provided by Fibres Recherche Développement®. According to the technical data sheet, fibers are 6 mm long with a diameter of 260 ±150 µm and their density is between 1.4 and 1.5 g/cm³. Concerning mechanical properties, Young's modulus is 36 ± 13 GPa, maximum stress is 750 ± 490 MPa and strain at break is 3.0 ± 1.9 %.

2.2. Methods

2.2.1. Processing

Polylactic acid granules were dried at 80°C during at least 24 hours and fibers were dried under vacuum at 120°C during 4h. The composite granules were obtained with a corotative twin-screw extruder (Clextral BC21). Screws are 900 mm long and the temperature profile is constant at 180°C. Then these semi-finished products were injected with an injection molding machine (Krauss Maffei KM50-180CX) into dogbones samples according to the standard ISO 527-2 1BA. The temperature profile is increasing up to 200°C and the mold is kept at 25°C.

2.2.2. Immersion in water

Two series of isothermal water aging were conducted for each material reference (PLA, PLA-L20 & PLA-L30): at 20°C and 35°C. For each, 10 samples per reference were immersed in water. Their mass, thickness, width and length were measured and half of the samples were subjected to modal analysis at given times up to 51 days.

2.2.3. Vibration analysis

The overall objective of this analysis consists in the study of the dynamical behavior of a structure thanks to its fundamental natural mode of vibration [8]. For this study, we expect this technique to determine the intrinsic elastic properties of the materials and more particularly its dynamic elastic modulus and damping coefficient.

Put in practice, samples are set in cantilever position (one end clamped, the other end free) with a free length of 60 mm (cf. *Figure 1*). The free end is stimulated by a short impulsion leading the sample to vibrate. The displacement during vibration is recorded by a laser sensor (SunX HL-C203F). This temporal response is then converted to a frequency response thanks to a fast Fourier transform (FFT). An interpolation of the Nyquist plot of the frequency response function enables to determine easily the eigen frequency and the damping factor of the first natural mode. This mode corresponds to the first flexural mode.

With finite element analysis software and based on the density and the geometry of the sample, it becomes possible to bring about the dynamic elastic modulus from the eigen frequency.

This unusual characterization technique is quick, non-destructive and easy to implement. However it requires knowing the density and the dimensions of the sample which may vary during aging.

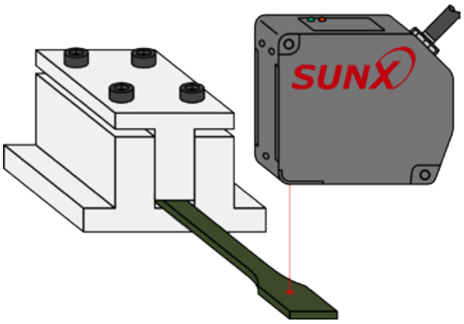

Figure 1 – Schematic representation of the set-up used to determine natural frequencies

2.2.4. Tensile creep tests

Given that the primary objective is to understand the long term behavior of materials in real use condition, the presence of mechanical solicitations is required. One can consider two types of long-term loadings: fatigue [9] and creep tests [10]. The latter was chosen. It consists in applying a constant stress on the sample and in this case in the tensile direction. In order to evaluate the evolution of the elastic properties in a degrading or non-degrading environment, the experiment protocol enables to release stress periodically and therefore to assess the elastic response of the material (cf *Figure 2*). The machine used for these tests is a Dartec model 100 kN on which has been adapted a control system from Tema Concept®.

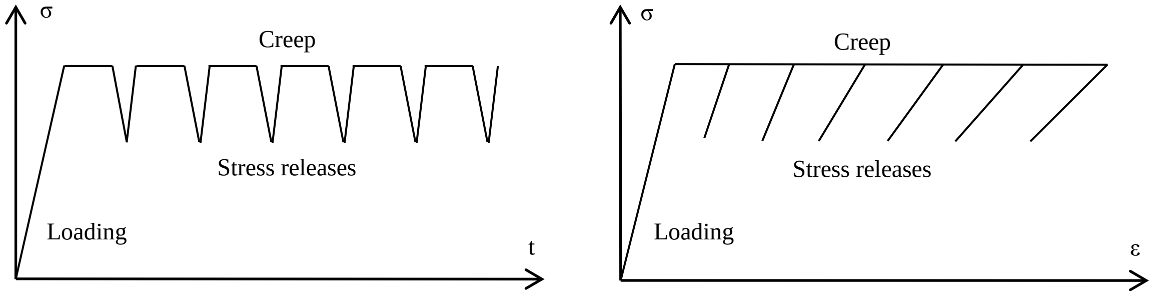

Figure 2 – Creep test with regular stress releases for elastic modulus assessment

Loading is set at 0.5 kN/s to reach the creep stress of 30 MPa. Then, 30 min later, stress is released down to 20 MPa and immediately raised again to 30 MPa (still at the same rate of 0.5 kN/s). The slope on the stress-strain graph during the release determines the elastic modulus. Creep is resumed during 30 min and this protocol is repeated until the break of the sample.

A set-up was design in order to allow these tests to be performed at constant relative humidity as well as underwater (cf. *Figure 3*). The tank in polycarbonate is waterproof and for an underwater test it just needs to be connected to a thermostat with water circulation (Julabo CF-31). For atmospheric tests, the top of the tank is covered with an elastomeric film thus reducing air transfer between the enclosure and the room.

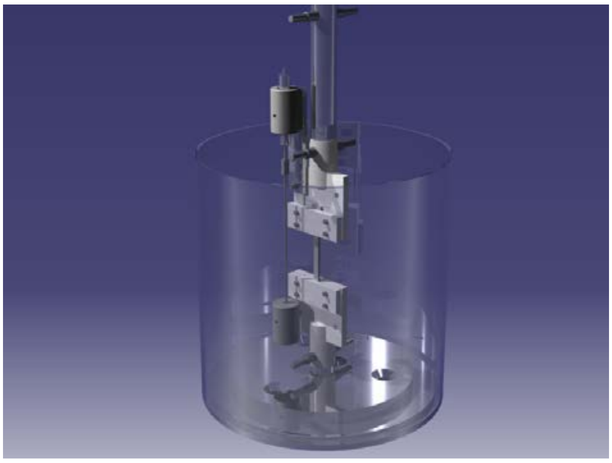

Figure 3 – Set-up for environmental creep tests

3. RESULTS AND DISCUSSION

3.1.1. Diffusion

Figure 4 shows experimental results for water uptake of the 3 references at 20°C and 35°C. Although standard deviation plots are plotted on the graph, it may be difficult to discern some of them because of the very good repeatability. The dashed lines correspond to the theoretical model of Fick [11] adapted to the sample geometry thanks to Comsol Multiphysics™, a finite element analysis software. Even though thickness of the samples is far less to be negligible compared to others dimensions, it seems that experimental sorption process is quite similar to infinite media diffusion.

Experimental water uptake displays a very good agreement with the Fickian diffusion, at least for the neat PLA. For composite the agreement is quite good at early times but then the curve sticks to a continuous gradual increase which does not reach equilibrium. This diffusion is called “pseudo-Fickian” diffusion [12]. In this case, one can assume materials undergo non-reversible damage, which may not be the case for the PLA.

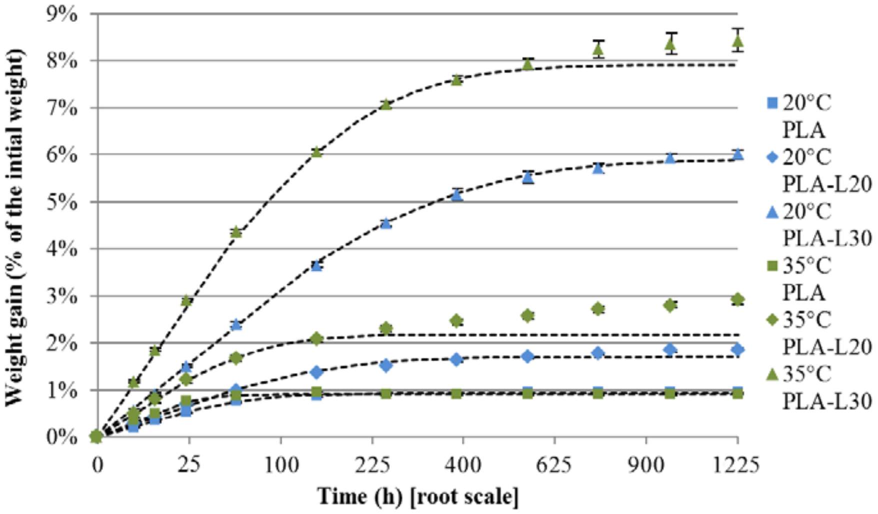

Figure 4 – Weight gain in flax/PLA composites (ISO 1BA injected samples) depending on immersion time in water and temperature (dashed lines represent the theoretical model of Fick)

Figure 5 represents volume gain during water uptake of the 3 references at 20°C and 35°C. Its assessment is based on the measures of the thickness, width and length of each sample. Obviously this technique presents the drawback not to be fully accurate. However the volume evolution of each sample is very similar to its weight gain. So it turns out to be logical the density does not vary appreciably (cf. *Figure 6*).

Yet it is possible to make some assumptions based on these results. Firstly PLA at both temperatures and PLA-L20 at 20°C seem to gain density. Actually, measures represent the bulk density thus including microscopic and mesoscopic cavities which can be filled with water during the diffusion process. This filling contributes to the increase of density since water is denser than air or void. On the contrary, the density of PLA-L30 composites decreases with immersion time. This decrease is even more important at 35°C. This may indicate that a non-reversible aging occurs inside the material. Some literature specifies PLA is prone to hydrolysis [13], [14]. So the composite is likely to release oligomers when macromolecular chains are cut by hydrolysis. The fact that the phenomenon is more significant at 35°C reinforces the idea that this supposition is correct. The phenomenon also occurs in the PLA-L20 at 35°C: even though density is constant, the two competitive processes take place into the material. Cavity filling raises bulk density while hydrolysis tends to reduce it.

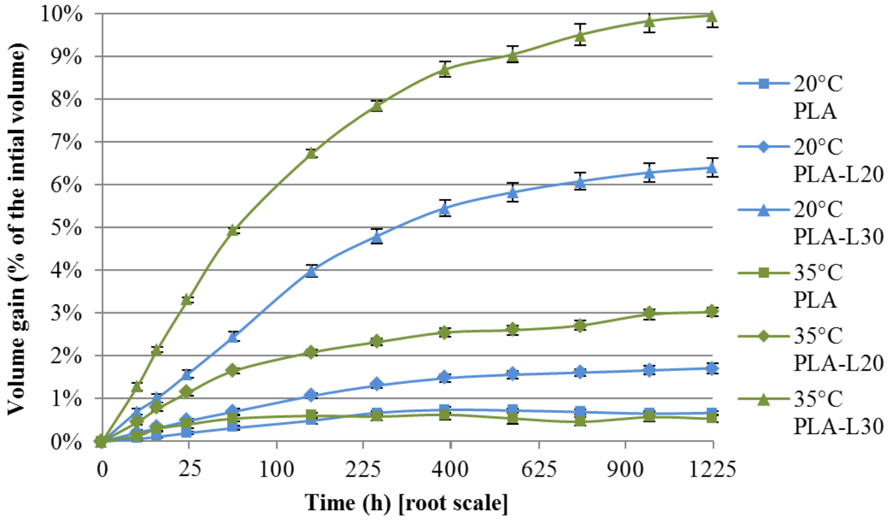

Figure 5 – Volume gain in flax/PLA composites (ISO 1BA injected samples) depending on immersion time in water and temperature

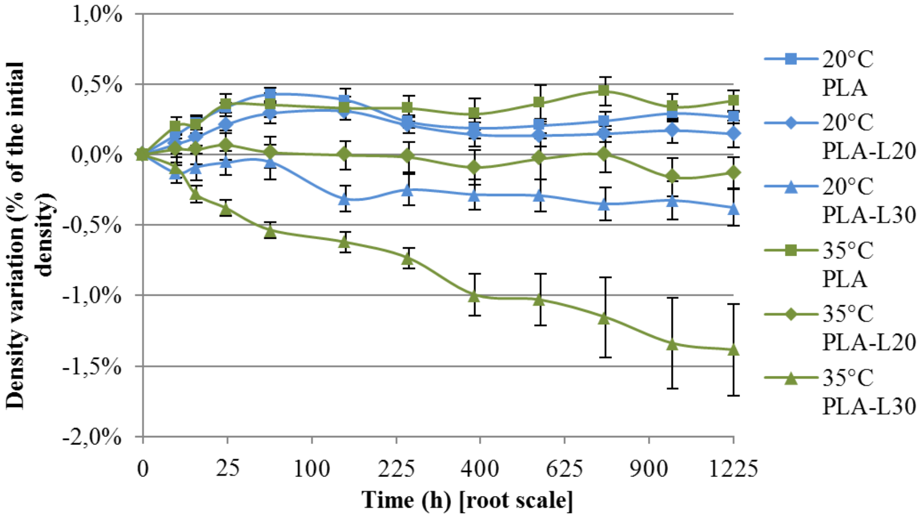

Figure 6 – Density variation in flax/PLA composites (ISO 1BA injected samples) depending on immersion time in water and temperature

The fitting of weight gain plots with the model of Fick enables to determine the two parameters: the diffusion coefficient (or diffusivity) and the water uptake at saturation (which corresponds to the maximum weight gain in the absence of non-reversible damage). Results are gathered in *Table 1*.

Naturally, diffusivity increases with temperature as it has been noticed in many papers [15], [16]. It might be surprising to notice that increasing the fiber content reduces the diffusivity. Yet it can be explained by the dependency of the diffusivity to the maximum water uptake.

Concerning the weight gain at saturation, temperature doesn't seem to have a real impact on PLA while differences are quite important for composites. However experimental results seem to deviate from the model of

Fick. Besides, this deviation matches the decrease of density. So it is legitimate to suppose that non-reversible degradation occurs.

D [mm²/h]	20°C	35°C
PLA	0,008	0,022
PLA-L20	0,0035	0,007
PLA-L30	0,0016	0,0027

M [%]	20°C	35°C
PLA	0,93%	0,91%
PLA-L20	1,65%	2,18%
PLA-L30	5,9%	7,9%

Table 1 – Diffusivity (D) and weight gain at saturation (M) for composites and neat PLA at 20°C and 35°C

Regarding the water content at saturation, it increases with the fiber content since fibers are highly hydrophilic [17]. Water is stored inside the fibers and likely at the interface between fibers and matrix. The high pressure gradient in the vicinity due to swelling could damage the interface thus leading to a decrease of mechanical properties. That will be assessed in the next part.

3.1.2. Viscoelastic behavior

Figure 7 shows the evolution of dynamic elastic modulus for the 3 materials at 20 and 35°C. Please note that characterization tests were carried out at room temperature just after samples were withdrawn from water.

At 20°C, the modulus of every reference decreases. This is the result of the plasticizing of polymer and the decrease of stiffness of natural fibers [18]. The stiffness of PLA is rather constant, so it corroborates the hypothesis of the absence of non-reversible damage.

Both composites stiffnesses tend toward equilibrium. Yet they are still stiffer than unreinforced PLA, meaning that the mechanical contribution of fibers is not negligible and the fiber/matrix interface is still partly effective.

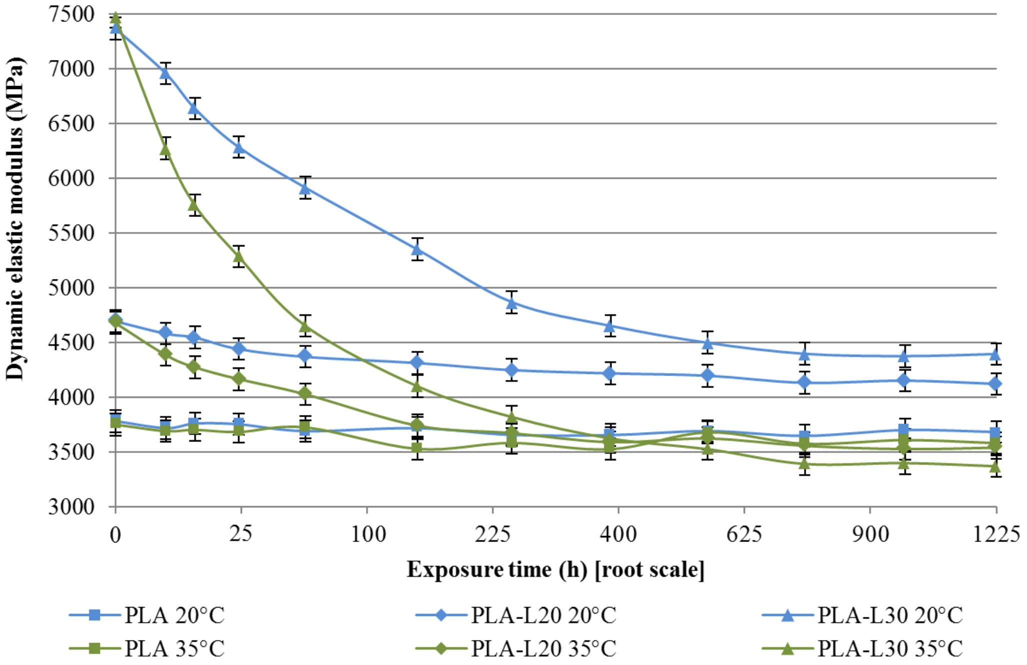

Figure 7 – Evolution of dynamic elastic modulus of flax/PLA composites versus exposure time in water and temperature

At 35°C, the decrease for each material is much more significant. However, all of them reach equilibrium for long-term. At this temperature, composites end up as stiff or even less that the unreinforced matrix. So it would mean that fibers do not contribute anymore to the mechanical behavior of the overall composites and that fiber/matrix interphase is totally unbound.

Clearly the influence of the temperature (only 15°C of difference) is very significant because it is close to glass transition temperature. And the more the composite is reinforced, the more the modulus drops.

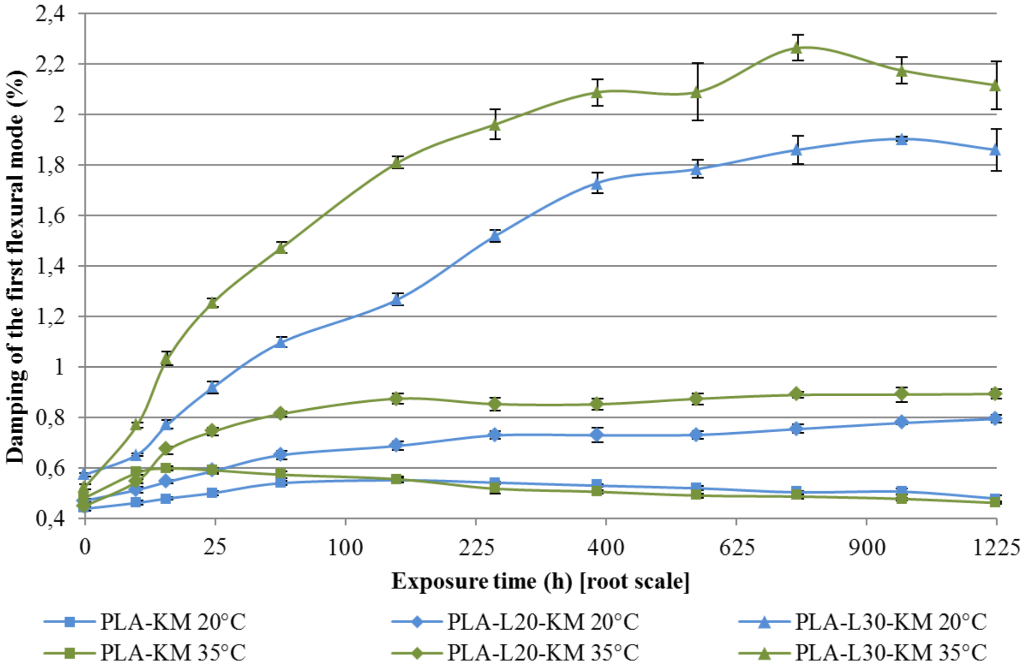

Figure 8 – Evolution of damping of flax/PLA composites versus exposure time in water and temperature

Figure 8 presents the evolution of damping from natural frequencies for the 3 materials at 20 and 35°C. Damping is controlled by dissipative factors such as friction at micro and mesoscale [19]. On the graph it appears that the more the material is reinforced, the more it dissipates energy. Temperature also plays an important role on damping. But this phenomenon is probably mainly controlled by the amount of water inside the material, at least for early times.

3.1.3. Creep

The objective of this part is to assess the mechanical properties of materials subjected to coupled hygrothermal/mechanical aging. The set up described in 2.2.4 is used to apply a constant stress on the sample in a controlled environment at 20°C and 50% of relative humidity. For now few trials have been made, so only unreinforced PLA is represented on *Figure 9*. The upper plot corresponds to the creep strain while the lower shows the evolution of elastic modulus over time.

Concerning the strain, the graph exhibits primary (when strain rate is decreasing) and secondary creep (when strain rate is constant) yet without tertiary creep. Yet, for the modulus, the decrease is monotonic throughout the test. However it cannot be certain why modulus is decreasing. Generally creep makes contribute the viscoelastic properties of the material. So is this damage caused only by the stress or a coupling due to the presence of water in the air (i.e. environmental stress cracking [20])? Further trials need to be carried out with different humidity levels to answer this question.

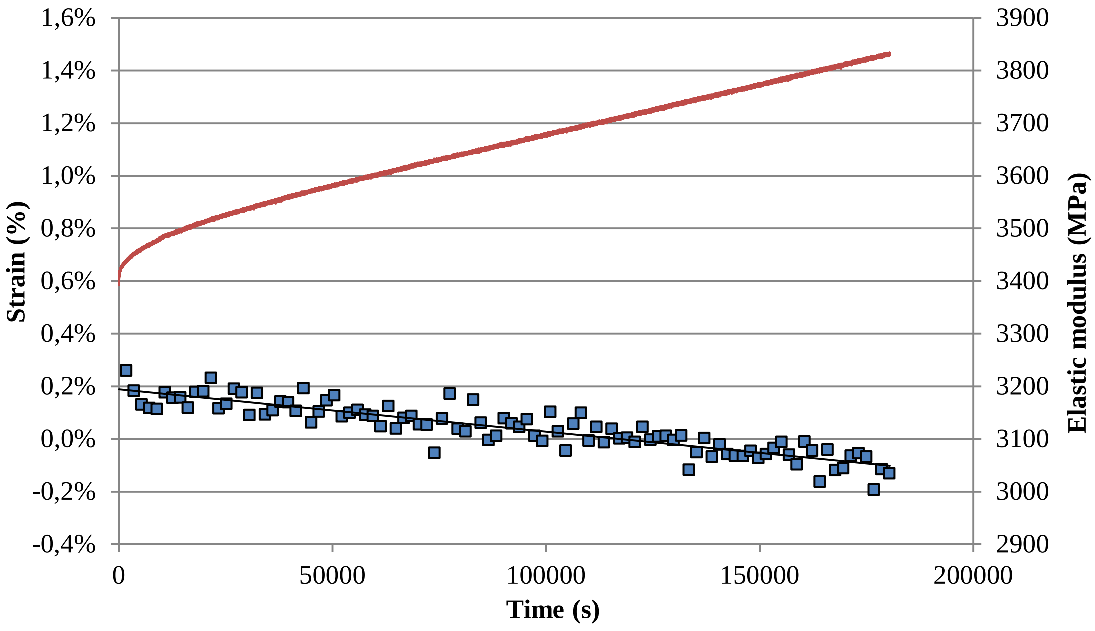

Figure 9 –Strain and evolution of elastic modulus of PLA during creep test at 20°C – 50%rh

4. CONCLUSION

This study examined the influence of water aging on physical and mechanical properties of polylactic acid/flax composites. Water and temperature turn out to have a major impact on both swelling and decrease of mechanical properties. The diffusion kinetics and the evolution of dynamic elastic modulus suggest that composites may have been irreversibly damaged for long duration at 35°C. However this shall be confirmed by mechanical testing after removal of all the water inside the materials.

Finally a decrease of the elastic modulus of PLA was highlighted during creep tests at 20°C and 50%rh. For now, no definitive conclusion can be made regarding the phenomenon. That is why other tests will be performed.

REFERENCES

[1] K. Oksman, “Natural fibres as reinforcement in polylactic acid (PLA) composites,” *Composites Science and Technology*, vol. 63, no. 9, pp. 1317-1324, Jul. 2003.

[2] B. Bax and J. Müssig, “Impact and tensile properties of PLA/Cordenka and PLA/flax composites,” *Composites Science and Technology*, vol. 68, no. 7–8, pp. 1601-1607, Jun. 2008.

[3] F. Vilaplana, E. Strömberg, and S. Karlsson, “Environmental and resource aspects of sustainable biocomposites,” *Polymer Degradation and Stability*, pp. 1-60, Aug. 2010.

[4] K. G. Satyanarayana, G. G. C. Arizaga, and F. Wypych, “Biodegradable composites based on lignocellulosic fibers—An overview,” *Progress in Polymer Science*, vol. 34, no. 9, pp. 982-1021, Sep. 2009.

[5] B. A. Acha, M. M. Reboredo, and N. E. Marcovich, “Creep and dynamic mechanical behavior of PP–jute composites: Effect of the interfacial adhesion,” *Composites Part A: Applied Science and Manufacturing*, vol. 38, no. 6, pp. 1507-1516, Jun. 2007.

[6] E. Vauthier, J. C. Abry, T. Bailliez, and A. Chateauminois, “Interactions between hygrothermal ageing and fatigue damage in unidirectional glass/epoxy composites,” *Composites Science and Technology*, vol. 58, no. 5, pp. 687-692, 1998.

[7] NatureWorks, “NatureWorks PLA Polymer 7000D,” 2005. .

[8] J.-S. Dupuy, “Identification des propriétés mécaniques de matériaux composites par analyse vibratoire,” Montpellier II, 2008.

[9] P. Rabbe, H.-P. Lieurade, and A. Galtier, “Essais de fatigue Partie I,” *Techniques De L’Ingénieur*, no. M4170, pp. 1-22, Oct. 2000.

[10] F. Saint-Antonin, “Essais de fluage,” *Techniques De L’Ingénieur*, no. M140, pp. 1-14, 1995.

[11] J. Crank, *The Mathematics Of Diffusion*, Second. Oxford University Press, 1975, pp. 1-421.

[12] Y. J. Weitsman, “Effects of Fluids on Polymeric Composites - A Review,” in *Comprehensive Composite Materials*, 2001, pp. 369-401.

[13] R. A. Cairncross, J. G. Becker, S. Ramaswamy, and R. O’Connor, “Moisture sorption, transport, and hydrolytic degradation in polylactide.,” *Applied biochemistry and biotechnology*, vol. 131, no. 1–3, pp. 774-85, Mar. 2006.

[14] C. S. Proikakis, N. J. Mamouzelos, P. A. Tarantili, and A. G. Andreopoulos, “Swelling and hydrolytic degradation of poly(D,L-lactic acid) in aqueous solutions,” *Polymer Degradation and Stability*, vol. 91, no. 3, pp. 614-619, Mar. 2006.

[15] S. Popineau, C. Rondeau-Mouro, C. Sulpice-Gaillet, and M. E. R. Shanahan, “Free/bound water absorption in an epoxy adhesive,” *Polymer*, vol. 46, no. 24, pp. 10733-10740, Nov. 2005.

[16] G. Z. Xiao and M. E. R. Shanahan, “Swelling of DGEBA/DDA epoxy resin during hygrothermal ageing,” *Polymer*, vol. 39, no. 14, pp. 3253-3260, Jun. 1998.

[17] B. S. Ndazi, “Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures,” *eXPRESS Polymer Letters*, vol. 5, no. 2, pp. 119-131, Jan. 2011.

[18] C. Baley, “Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase,” *Composites Part A: Applied Science and Manufacturing*, vol. 33, no. 7, pp. 939-948, Jul. 2002.

[19] M. Meyers and K. Chawla, *Mechanical Behavior of Materials*. Cambridge: Cambridge University Press, 2009, p. 882.

[20] J. Arnold, “The influence of liquid uptake on environmental stress cracking of glassy polymers,” *Materials Science and Engineering A*, vol. 197, no. 1, pp. 119-124, Jun. 1995.