EXPERIMENTAL CREEP ANALYSIS OF BIODEGRADABLE POLYMER MATRIX NANOCOMPOSITES FOR ACL REPLACEMENT

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Abstract
The evolution of materials used for anterior cruciate ligament (ACL) ruptures repair has been remarkable, currently emerging from cooperation between Mechanical Engineering, Biomaterials and Tissue Engineering. Currently, regarding this application, biodegradable polymers like polylactic acid (PLA) have been researched as a solution, however its mechanical characteristics must be improved with reinforcements, namely its mechanical resistance to fatigue, preventing laxity or rupture of the device.
Concerning to PLA viscoelastic behaviour influence on these device issues, it is presented a experimental creep mechanical study of some PLA-matrix nanocomposites reinforced with carbon nanoparticles, particularly carboxyl functionalized carbon nanotubes (PLA/MWCNT-COOH), showing permanent strain reduction accumulated on nanocomposites.

1. Introduction

Anterior cruciate ligament's (ACL) chemical composition and geometry, along with its mechanical properties are key issues during a medical device development. Similarly to other biological structures, ACL is a composite and dense material with an hierarchical arrangement very complex and of hard mimic [1,2] that supports multiaxial stress and several deformations [3].

Currently there are available solutions for ACL replacement both natural and artificial for a permanent approach [4-7], but with some limitations. Attending to its biocompatibility and rate of success, physicians predominantly choose to apply natural replacers, as autografts and allografts, however they have limited availability and need for harvest surgery, as well as donor area shortage, rejection, disease transfer and high harvesting costs [8, 9]. So, there is an impulse for artificial solutions research [4] and for a temporary approach development which intends to allow ACL regeneration around a biodegradable scaffold during ACL recovery period, while this will degrade, ending up disappearing. This approach begins by finding an

appropriate material within the ACL functionality as a biodegradable scaffold and then combines it with Tissue Engineering techniques, like growing factors.

For this approach, biodegradable polymers, particularly aliphatic polyesters [10], have been studied such as PLA [11], PGA [12], PDO [12] and biodegradable copolymers also, like PLA/PCL, PLA/PGA [10, 12] and PLA has already FDA's approval for medical devices use. These were developed during 60's decade as biomaterials, due to its high biocompatibility and controllable degradation rates and have properties as a semicrystalline structure (37% of crystallinity), hydrophobicity [13], with and high elastic modulus (4,8GPa) and a glass transition temperature between 60-65ºC [14]. All these properties depend on molecular weight and production parameters [15-17].

However attending to some previous results [10], there is the need to mechanically reinforce some of these polymers and copolymers. Plastic deformation is the main cause for medical devices failure [4], hence is important to analyze time-dependent deformation behaviour of the polymers and nanocomposites, by evaluate creep response [18].

Some attempts have been made to reinforce PLA mechanical properties, through copolymers [18-20] and composites fabrication [19, 20]. Recently, some solution for composite polymer matrix has been researched, with carbon nanostructures such as graphene and carbon nanotubes (CNTs) [21]. CNTs have extremely good mechanical properties due to their strong sp^2 carbon-carbon bondings [22], with their elastic modulus varying between 1TPa and 1.2TPa and their tensile strength up to rupture between 50 and 200GPa [23].

Due to their great mechanical and physical properties, CNTs are considered as the ideal reinforcement fillers on composites, once a small amount of it could promote significant increase on the mechanical properties of the polymers [44]. This increase could be larger considering an high interfacial adhesion between CNTs and the polymer [24], that could be developed by the use of functionalized CNTs [25-29], with hydroxyl and carboxyl functional groups on CNTs [30, 31] walls and high dispersion production methods [32, 33].

Several studies indicate a real reinforce of the scaffold structure [34-37] [38], attending to the load transfer accuracy between nanotubes and the polymer which determines the mechanical performance of the composite [39-43]. Also existent experimental results showed an increase of the creep resistance by adding CNTs to polymeric matrices for different stress levels [18, 44].

To analyze time dependent creep behaviour of PLA and PLA/functionalized CNT nanocomposites here is an initial study of their plastic deformation.

2. Materials and Methods

2.1. Materials

Poly(lactic acid) (PLA) (Ingeo™ 2002D) with 4% D-lactide and 96% L-lactide content and molecular weight around 121,400 gmol^{-1}, was purchased from Natureworks LLC (Minnetonka, USA).

Short thin multi-walled carbon nanotubes with surface modified COOH (CNT), having dimensions of 9.5 nm average diameter and less than 1 μm average length, and more than 95% carbon purity was obtained from Nanocyl, Belgium (grade Nanocyl™ NC3151). These were produced via catalytic chemical vapor deposition (CCVD). The density for the MWCNT batch used was about 106 kg/m^3.

2.1.1 Specimens preparation

PLA was prepared by melt blending in a universal torque rheometer Plastograph™ (Brabender®), with mixing parameters of 190ºC as mixing temperature, 50 min^{-1} as mixing speed and 10 minutes as mixing time.

Resorting PLA polymer-matrix/CNT nanocomposites mixtures were prepared by the same method, melt blending, in the same rheometer Plastograph™, with same mixing parameters. It was added PLA to the Plastograph™ and the respective weight percentages of CNT described in Table 1.

PLA and PLA nanocomposites	Nanofiller	PLA [wt%]	Nanofiller [wt%]
PLA	-	100	0
PLA/CNT0.2	–COOH functionalized carbon nanotubes	99.8	0.2
PLA/CNT0.3	–COOH functionalized carbon nanotubes	99.7	0.3
PLA/CNT0.5	–COOH functionalized carbon nanotubes	99.5	0.5
PLA/CNT0.7	–COOH functionalized carbon nanotubes	99.3	0.7
PLA/CNT1	–COOH functionalized carbon nanotubes	99	1

Table 1. PLA and PLA nanocomposites produced for experimental tests

Thin films were prepared by compression moulding using the produced mixtures in a hot plates press. Both plates of the press were monitored and were initially heated up to 170ºC. Each mixture was placed between Teflon® plates with a square mould of 150 mm side and 0.3 mm thickness inside the press, during 15 minutes and then all the set was pressed during 2 minutes with around 1 bar pressure. Resulting into 0.43 ± 0.005 mm average thickness thin films from where specimens were cut for tensile mechanical tests.

The specimens were cut in a rectangular format with a length of 80 mm and 10 mm width, being the gauge length 50 mm.

2.2. Methods

2.2.1. Tensile tests

Firstly, tensile tests up to rupture were made in an Instron ElectroPuls E1000, with a load cell of 2kN, under displacement control at a rate of 2 mm/min. Three specimens were tested for tensile and creep tests. During tensile tests maximum tensile strength was determined for each nanocomposite and for accurate measurements it was used a non-contact optical measurement technique, namely Feature Tracking Method [45] for both tests type.

2.2.2. Creep tests

Creep tests were made under load control, for several levels of maximum tensile strength, particularly 10% (T1), 30% (T2), 50% (T3) and 70% (T4). The increasing load ramp was of 2.5N/s up to each stress level and kept constant at that level during 600 seconds. Then load decreases during another 600 seconds until it resets (Figure 1). All tests were made at temperature of 20ºC.
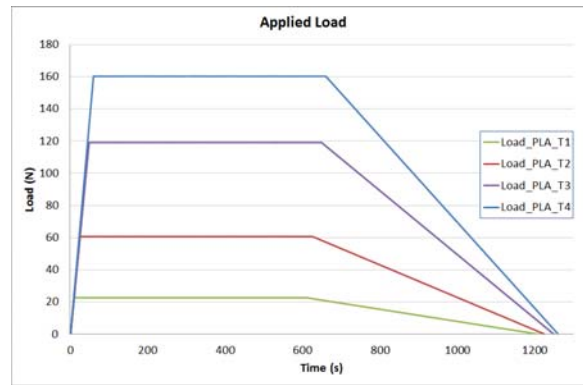
Figure 1. Example of applied load on each stress level tested for PLA

3. Results and Discussion

3.1.1. Tensile tests

Attending to possible small deviations on the specimens dimensions, it was considered the minimum value of the three specimens' maximum strength results for creep tests. Tensile tests results are described in Table 2.

Specimen	Maximum Stress [MPa]	% of Maximum Stress [MPa]			
		10%	**30%**	**50%**	**70%**
PLA	50.109±2.932	5.011	15.033	25.055	35.076
PLA/CNT0.2	47.575 ±2.132	4.758	14.273	23.788	33.303
PLA/CNT0.3	49.346±4.323	4.935	14.805	24.673	34.542
PLA/CNT0.5	45.944±0.337	4.594	13.783	22.972	32.161
PLA/CNT0.7	47.959±1.232	4.796	14.388	23.979	33.571
PLA/CNT1	45.072±1.151	4.507	13.522	22.536	31.551

Table 2. Maximum stress and % stress levels for each specimen

3.1.2. Creep tests

3.1.2.1. Strain Behaviour and Residual Strain

Attending to primary creep, it is possible to verify on Figure 2, that for PLA and PLA/CNT nanocomposites, there is an accumulated strain at the end of the test, and this residual strain has higher values according to higher stress levels. During the constant load phase strain increases, being constant for lower stress levels and changing this behaviour for higher stress levels
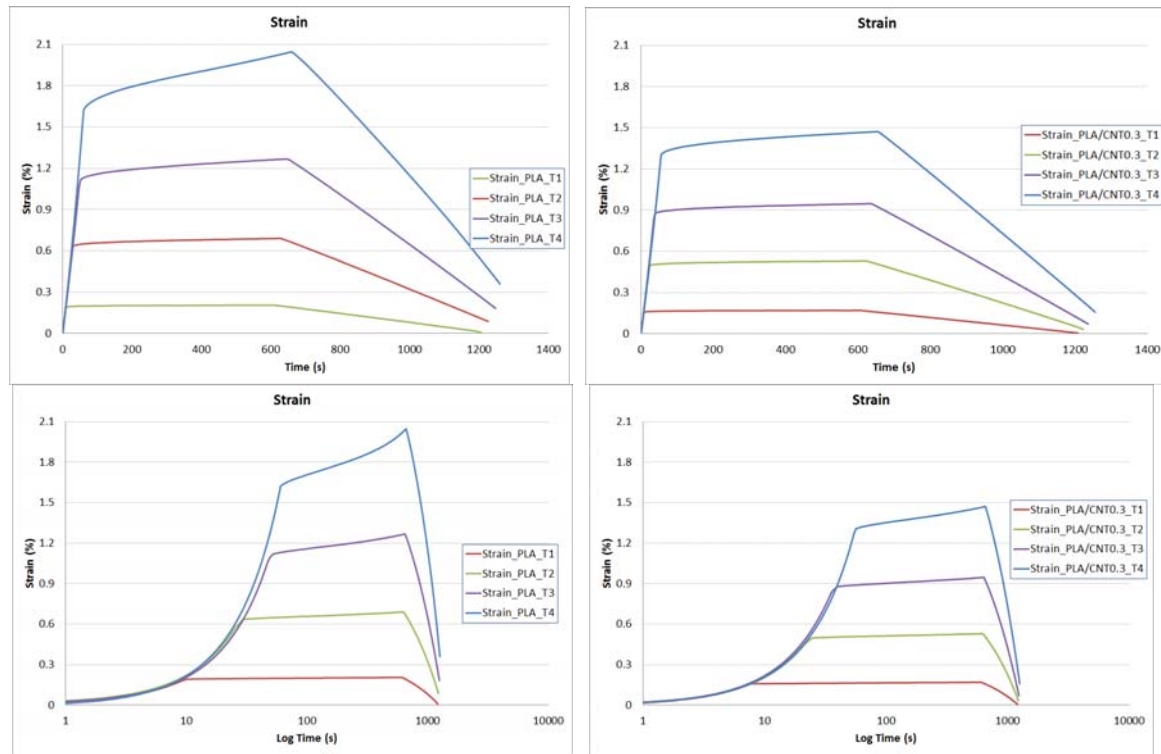
Figure 2. Examples of experimental strain results for PLA and PLA/CNT0.3, in strain vs time and strain vs log time plots (bellow).

For PLA and all PLA/CNT nanocomposites and for all level tests, strain behaviour was determined and it is possible to see that almost in every stress level there is a decrease on residual strain of PLA/CNT nanocomposites comparing to PLA (Tables 3 and 4), showing an increase of the creep resistance. However PLA/CNT0.2 and PLA/CNT0.3 for 10% of maximum stress showed and increase comparing to PLA.

Specimen	Mean residual strain [%]			
	10%	30%	50%	70%
PLA	0.0326±0.0066	0.0788±0.0309	0.0988±0.0454	0.2350±0.1289
PLA/CNT0.2	0.0357±0.0115	0.0318±0.0095	0.0479±0.0046	0.1044±0.0535
PLA/CNT0.3	0.0394±0.0077	0.0437±0.0100	0.0450±0.0040	0.0778±0.0102
PLA/CNT0.5	0.0324±0.0124	0.0246±0.0031	0.0535±0.0096	0.1282±0.0209
PLA/CNT0.7	0.0263±0.0039	0.0360±0.0064	0.0454±0.0050	0.1135±0.0197
PLA/CNT1	0.0288±0.0012	0.0454±0.0163	0.0563±0.0281	0.1066±0.0131

**Table 3.** Mean residual strain for all specimens and for the four stress levels tested.

Specimen	Variation of mean residual strain relatively to PLA [%]			
	10%	30%	50%	70%
PLA/CNT0.2	+9.57	-59.68	-51.50	-55.58
PLA/CNT0.3	+20.79	-44.53	-54.42	-66.90
PLA/CNT0.5	-0.59	-68.75	-45.86	-45.46
PLA/CNT0.7	-19.28	-54.34	-54.11	-51.70
PLA/CNT1	-11.76	-42.34	-43.04	-54.66

Table 4. Variation of mean residual strain for all PLA/CNT nanocomposites specimens and for the four stress levels tested comparing to PLA specimens.

3.1.2.2. Strain Experimental Fitting Model

For higher stress levels (50 and 70%) it was possible to model primary creep with potential law fitting (1) with high accuracy (Figure 3), with mean R^2 around 0.997, like:

$$\varepsilon = At^n \tag{1}$$
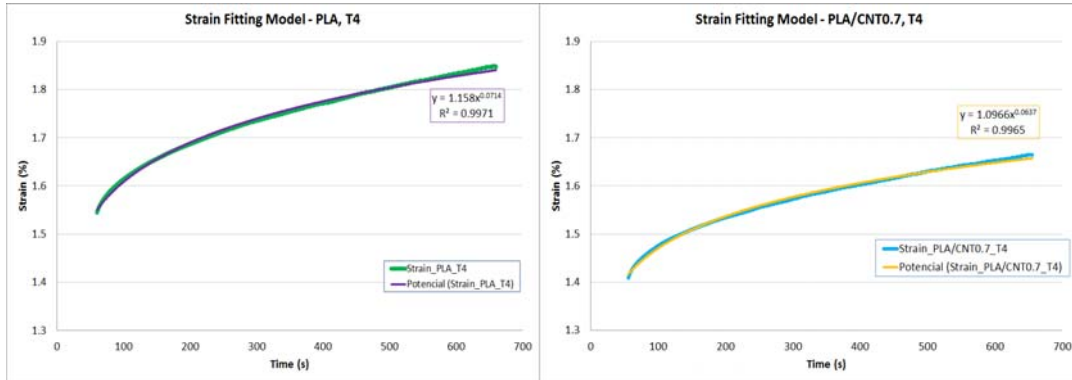
Figure 3. Example of strain potential fitting model for PLA and PLA/CNT0.7 nanocomposites for higher stress level.

3.1.2.3. Creep Modulus

Analysing creep modulus, Figure 4 shows for PLA and PLA/CNT nanocomposites a similar constant behaviour, pointing to a linear viscoelastic behaviour, for 10%, 30% and 50% of maximum stress. For a higher stress level creep modulus increases with time, confirming nonlinear viscoelasticity of PLA and PLA/CNT nanocomposites.
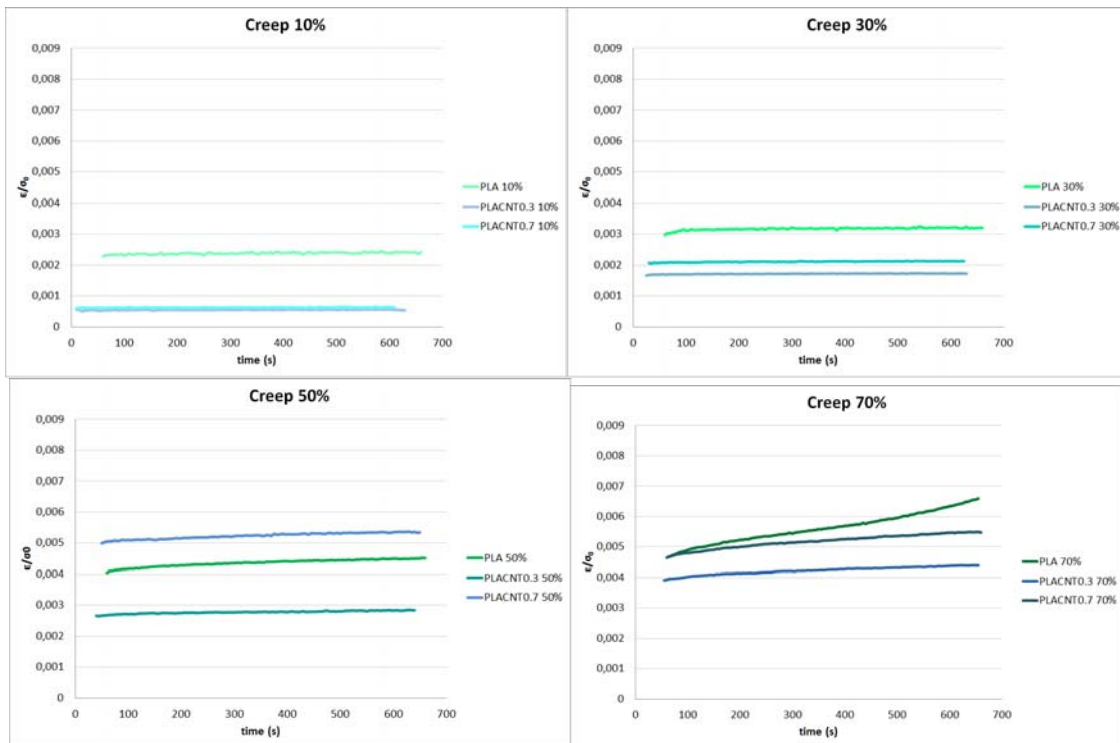
Figure 4. Creep modulus behavior for PLA, PLA/CNT0.3 and PLA/CNT0.7 nanocomposites for four stress levels.

4. Conclusions and Future work

It was found PLA/CNT nanocomposites accumulate less permanent strain for all levels of stress tested and analysing creep compliance for these nanocomposites it seems that they present a less viscous and more elastic relatively to PLA (Figure 3). For 70% of maximum stress and for PLA/CNT nanocomposites specimens residual strain decreases between 46% and 67% comparing to PLA.

A potential law can describe, with high accuracy, strain behaviour during constant load regime for high stress levels.

For PLA and all PLA/CNT nanocomposites creep modulus is constant, until 50% of maximum stress is achieved, included, hence it is possible to considered up to this value, that specimens showed linear viscoelasticity. At 70% of maximum stress, creep modulus indicates nonlinear viscoelasticity. For every level creep modulus is higher for PLA than for PLA/CNT nanocomposites.

To preview this behaviour, Burger's model will be applied to this experimental data, showing already in preliminary tests to be an adjusted model for PLA an PLA/CNT nanocomposites.

Acknowledgements

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