# RELIABILITY IN ECODESIGN OF INTERIOR PARTS IN AEROSPACE AND AUTOMOBILE INDUSTRY USING BIODEGRABLE THERMOPLASTICS

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*Abstract. There are many biodegradable polymers commercially available to produce a great variety of plastic interior parts to be used automobiles, trains and airplanes in order to obtain "green products", following eco-design philosophies.*
*Reliability of a product may be defined by its ability to fulfill requirements during time. Biodegradable plastics can present short term performances similar to conventional plastics. Though, performance of a biodegradable product will decrease during time, due to hydrolytic degradation, and it should be enough for the predicted use, during all its life cycle. However, the mechanical behavior of biodegradable materials along its degradation time is still an unexplored subject.*
*In this work it is considered a three-dimensional viscoplastic model. It enables to simulate the monotonic tests of a biodegradable structure loaded under different strain rates, and also the hysteresis effects during unloading-reloading cycles at different strain levels. Furthermore a parametric study is presented, showing the evolution of the material model parameters during the hydrolytic degradation, and analyzing those parameters more sensible to this process. The investigated model was able to predict well the experimental results of a blend of polylactic acid and polycaprolactone (PLA-PCL) in the full range of strains until rupture during hydrolytic degradation.*

*Keywords: ecodesign, constitutive models, viscoplastic, biodegradable, plastics*

## 1. INTRODUCTION

Several biodegradable polymers are used in many commodity products with short life cycle, each of them with suitable properties according to the application. Different mechanical properties and degradation rates are possible among these polymers, for many applications in products used during relatively short periods. However, each of these may have some shortcomings, which restrict its use in a specific application, due to inappropriate stiffness or degradation rate. Blending, copolymerization or composite techniques are extremely promising approaches, which can be used to tune the original mechanical and degradation properties of the polymers (Aslan *et al.*, 2000) according to the application requirements, enabling a range of mechanical properties and degradation rates. The most popular and important class of biodegradable synthetic polymers are aliphatic polyesters, such as polylactic acid (PLLA and PDLA), polyglycolic acid (PGA), polycaprolactone (PCL), polydioxone (PDO), polyhydoxyalkanoates (PHA's) and polyethylene oxide (PEO) among others. They can be processed as other thermoplastic materials. Hydrolytic and/or enzymatic chain cleavage of these materials leads to α-hydroxyacids, which, in most cases, are ultimately eroded and assimilated in a composting environment. Contrarily to conventional plastics based on oil, bioplastics are obtained from renewable resources. Monomers hydrocarbons are obtained by processing agricultural products (like sugar, potato, soya, corn, etc.) or from genetic modified bacteria cultured in optimized environments. Hence, their degradation in composting or their combustion results in $CO_2$ emissions that were naturally accumulated by photosynthesis, and would occur any way as consequence of source plants degradation. This way the carbon cycle is a closed loop. Hence, biodegradable plastics claim clear environmental advantages, mainly in their final stage of life (waste disposal), which can clearly be evident through life cycle assessment.

Performance of a product is mostly conditioned by the materials selection and dimensioning. For a biodegradable product, strength, maximum strain and toughness will decrease along its degradation, and it should be enough for the predicted use. Exploratory experiments in degradation environment models that represent the service conditions can be carried out as a preliminary step to assess the performance of a biodegradable product design. However, such studies represent a costly method of iterating the product dimensioning. It is very important to mention that, nowadays, there isn't an established scientific method to develop a product made from biodegradable polymer. Thus, scientific

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contributions in this direction can aid the development of reliable biodegradable components for automobiles, trains and airplanes, according to the quality standards demanded by those industries.

The failure criteria for maximum strength as a function of degradation time have traditionally been modeled according to a first order kinetics. The dimensioning of these components can be complex, not only because the mechanical properties evolve during degradation, but also because these biodegradable materials cannot be modeled using only elastic constitutive equations (Soares, 2008). In more precise terms, the response of an elastic material implies that the loading and unloading paths coincide, the material responds instantaneously to an applied load. This behavior is time-independent and the material returns to its former unloaded configuration upon the removal of external loads. However, for example, Soares (2008) and Grabow *et al.* (2007) verified the nonlinear viscoelastic characteristics of PLA. Also, the experimental results for the researched biodegradable material (PLA-PCL blend in proportion 90:10), presented in a previous work (Vieira *et al.*, 2013) clearly demonstrate the non linear time-dependent mechanical behavior. The mechanical load tests were carried out, considering not only monotonic tensile tests at different strain rates, but also cycle tensile tests with unload and reload at different strain levels. Therefore, time-dependent constitutive models are required to simulate all those phenomena.

A constitutive model for a mechanical analysis is a relationship between the response of a body (for example, strain state) and the stress state due to the forces acting on the body, which can include the environmental effects. A wide variety of material behaviors can be described with a few different classes of constitutive equations. And the existing models can be divided into two categories: the equilibrium models and the time-dependent models (Bergström and Boyce, 1998). Several constitutive models have been proposed for non-degraded polymers and elastomers. Most of the early work (Flory, 1977; James and Guth, 1943; Treloar, 1975; Wall and Flory, 1951) was devoted to the prediction of the equilibrium response. One of the most successful models for this problem is the 8-chain network model developed by Arruda and Boyce (1993a).

It is known that the stress in a biodegradable polymer after being subjected to a step in the applied strain will relax towards an equilibrium state (Miller and William, 1984). This equilibrium state can be represented by linear elastic or non linear elastic models, such as elasto-plastic or hyperelastic models. The response of an elastic or hyperelastic material implies that the loading and unloading paths coincide. Mechanical properties of biodegradable plastics are commonly assessed within the scope of linearized elasticity, despite the clear evidence that they can undergo large strains before breaking. Other inelastic or hyperelastic models are required to model those situations. Hence, given the nature of biodegradable polymers, classical models such as the neo-Hookean and Mooney-Rivlin models, for incompressible hyperelastic materials, have been used to predict mechanical behavior until rupture of non-degraded PLA (Garlotta, 2001; Lunt, 1998) under quasi-static monotonic loading. However, those approaches neglect changes in the properties of the material during degradation process. In the case of elasto-plastic models, after unloading phase, the material returns to an equilibrium sate, which includes some plastic strain. These types of models show at least one sliding element in its model formulation. Hence, the loading and unloading paths do not coincide. Although, these approaches neglect the time-dependent mechanical behavior, they can simulate the equilibrium response.

To account time dependency, dissipative elements must be used in the model formulation. The simplest viscoelastic models consider a linear combination of springs (using the Hooke's law) and dashpots (using Newtonian damper with linear viscosity). The classical examples of these simple models are the Maxwell and Kelvin–Voigt models, in which spring and dashpots are organized in series or in parallel, respectively. The elastic component is modeled using a single material parameter $E$ (Young modulus) according to the Hooke's Law, $\sigma = E\varepsilon$. Analogously, the dissipative element uses a single material parameter $\eta$ (viscosity) according to the equation $\sigma = \eta \, d\varepsilon/dt$.

More complex variants of these simple models can be found at the literature (Bardenhagen *et al.*, 1997; Arruda and Boyce, 1993b; Boyce *et al.*, 1988; Bergström *et al.*, 2002; Drozdov and Gupta, 2003; Fancello *et al.*, 2002; Harren, 1995; Hasan and Boyce, 1995; Hausler and Sayir, 1995; Holzapfel, 1996; Johnson *et al.*, 1995; Lubarda *et al.*, 2003; O'Dowd and Knauss, 1995; Reese and Govindjee, 1998; Runbin, 1987; Zdunek, 1993). These models can simulate the non linear viscoelastic, viscoplastic and hysteretic nature of polymers. These models are based on the same concept of networks, combining elastic, sliding and dissipative elements, in order to simulate the equilibrium response of the material and the time-dependent deviation from equilibrium state. However, those approaches have been applied to predict the mechanical behavior of polymers neglecting changes in the properties of the material during the hydrolytic degradation process. Therefore, it is possible to find only few recent scientific contributions about this issue in the literature, mainly concerning biodegradable polymers.

Regarding the challenge presented above, in the following section of this work, the degradation process is discussed, demonstrating how these phenomena can be mathematically modeled. After that, a three-dimensional viscoplastic model developed by Bergström and Boyce (1998) is analyzed in terms of its potential and limitations to represent a complex load case scenario in a biodegradable material. Since this model assumes that the mechanical behavior is divided into an equilibrium network and a non-linear time-dependent network, it enables to simulate the monotonic tests of a biodegradable structure loaded under different strain rates. Also, it is possible to predict the hysteresis effects during unloading-reloading cycles at different strain levels. Furthermore a parametric study is presented, showing the evolution of the material model parameters during the hydrolytic degradation, and analyzing those parameters more sensible to this process. The investigated viscoplastic model was able to predict well the experimental results of a blend

of polylactic acid and polycaprolactone (PLA-PCL) in the full range of strains until rupture during hydrolytic degradation. Finally, a method is proposed, based on this analysis, to simulate the three-dimensional viscoplastic mechanical behavior during hydrolytic degradation.

## 2. HYDROLYTIC DEGRADATION

Usually, the most important degradation mechanism of biodegradable polymers is chemical degradation via hydrolysis (Göpferich, 1996). Due to hydrolytic chain scission, which occurs in the polymeric macromolecules, and the consequent reduction of molecular weight, the mechanical response of a biodegradable polymeric product will evolve during this process. Hydrolysis rates are affected by the temperature or mechanical stress, molecular structure, ester group density as well as the relative humidity of the surrounding media. The most important is its chemical structure and the occurrence of specific bonds along its chains, like those in groups of esters, ethers, amides, etc. which might be susceptible to hydrolysis (Nikolic *et al.*, 2003; Herzog *et al.*, 2006).

Another important distinction must be made between erosion and degradation. Both are irreversible processes. On one hand the degree of erosion is estimated from the mass loss, or $CO_2$ conversion and it occurs mostly in composting. On the other hand, the degree of degradation occurs during service with negligible mass loss, and can be estimated by measuring the evolution of molecular weight, by gel permeation chromatography (GPC), or the tensile strength evolution (by universal tensile testing). Hence the hydrolytic degradation process, where the mechanical properties are significantly reduced, is included on the erosion process.

### 2.1 Diffusion

Generally, a biodegradable polymeric product is in service on an environment with some relative humidity. Generally, polymers are prone to absorb water, up to a saturation level of water concentration. This maximum level of water concentration and the diffusion rate depends on the hydrophilicity of the polymer, its crystalline degree, temperature and the relative humidity of the media. The penetrating water creates a negative gradient of water concentrations from the surface to the centre, as expected from a pure diffusion viewpoint. Therefore, one can consider that hydrolysis of ester bonds is heterogeneous along the volume from the beginning. In the case of interior parts in aerospace and automobile industry, diffusion of water occurs simultaneously with the degradation process. However, this gradient vanishes when the specimen saturates. Furthermore, water acts as a plasticizer, lowering the glass transition temperature and softening the material.

The water concentration ($w$) along the three directions ($x$, $y$ and $z$), and during the incubation time ($t$), is determined using Fick's equation 1, presented for 3D:

$$\frac{dw}{dt} = D_1 \frac{\partial^2 w}{\partial x^2} + D_2 \frac{\partial^2 w}{\partial y^2} + D_3 \frac{\partial^2 w}{\partial z^2} \tag{1}$$

In the case of isotropic polymers, diffusion has no preferential direction, and $D_1=D_2=D_3=D$. The diffusion rate $D$ of the material can be determined by measuring moisture absorption increased weight during incubation.

### 2.2 Hydrolysis

The macromolecular skeleton of many polymers comprises chemical bonds that can go through hydrolysis in the presence of water molecules, leading to chain scissions. In the case of aliphatic polyesters, these scissions occur at the ester groups. A general consequence of such process is the lowering of the plastic flow ability of the polymer, causing the change of a ductile and tough behavior into a brittle one. In figure 1, it is presented a scheme of the most common hydrolysis mechanism. Each polymer molecule, with its own carboxylic and alcohol end groups, is broken in two, randomly in the middle at a given ester group. Hence, the number of carboxylic end groups will increase with degradation time, while the molecules are being splited by hydrolysis.

Hydrolysis has traditionally been modeled using a first order kinetics equation based on the kinetic mechanism of hydrolysis, according to the Michaelis–Menten scheme (Bellenger *et al.*, 1995). According to Farrar and Gillson (2002), the following first-order equation 2 describes the hydrolytic process related to the carboxyl end groups ($C$), the hydrolysis rate constant ($k$), ester concentration ($e$) and water concentration ($w$), during the degradation time ($t$):

$$\frac{dC}{dt} = kewC \tag{2}$$

Using the molecular weight, and since the concentrations of carboxyl end groups are given by $C=1/M_n$; the equation 2 becomes equation 3:

$$M_{n_t} = M_{n_0} exp^{-kewt} \qquad (3)$$

where $M_{nt}$ and $M_{n0}$ are the number-average molecular weight, at a given time $t$ and initially at $t$=0, respectively. This equation leads to a relationship $M_n = f(t)$. However, in the design phase of a biodegradable product, it is important to predict the evolution of mechanical parameters, like tensile strength, instead of molecular weight. It has been shown by Vieira *et al*. (2011a) that the fracture strength follows the same trend as the molecular weight, described by equation 4:

$$\sigma_t = \sigma_0 \, exp^{-kewt} \qquad (4)$$



Figure 1. Acid catalyzed hydrolysis mechanism (Vieira *et al.*, 2011a)

The hydrolytic damage was defined by Vieira et al. (2011a), according to equation 5:

$$d = 1 - \frac{\sigma}{\sigma_0} == 1 - \frac{M_{n_t}}{M_{n_0}} = 1 - exp^{-kewt} \qquad (5)$$

Temperature will increase the hydrolysis rate constant $k$, which is associated to the probability of bond scissions, due to excitement of the molecules. The influence of the mechanical environment in the degradation rate has been also reported by some researchers (Miller and William, 1984). Similarly to temperature, stress also increases the probability of bond scissions. In this early stage of erosion, when mechanical strength droops significantly, also the ester concentration $e$ is nearly constant, because the macromolecules remain macro, despite the scissions, which occur randomly in the ester groups (Göpferich and Langer, 1993). Therefore, hydrolytic damage will depend not only on the biodegradation time, but also on the water concentration and the hydrolysis kinetic constant, which depend on the geometry, the stress state and the temperature and relative humidity of the surrounding environment. Then hydrolytic damage will be a local internal variable, which varies along the volume and must be calculated previously at each material point and at each biodegradation step. On one hand, the slow diffusion promotes heterogeneous concentration of water. On the other hand, the three-dimensional stress field will evolve during the degradation process due changes in the constitutive relation in consequence of the degradation process. The hypothesis of homogeneous degradation, which considers instant diffusion, may be valid for specimens immersed in water. In these cases, diffusion is much faster than the hydrolytic degradation process. Since this case is easier to analyze, in this work we studied the degradation under water without any load, to study the evolution of the material parameters of a viscoplastic constitutive model as function of the hydrolytic damage. To simulate the evolution of the mechanical behavior of biodegradable polymers, the constitutive models must be adapted accordingly to hydrolytic damage.

## 2.3 Review of the methods to simulate the mechanical behaviour during hydrolytic degredation

Recent developments of hyperelastic constitutive models enable the modeling of biodegradable structures during degradation (Soares *et al.*, 2010; Vieira *et al.*, 2011b) considering that the constitutive model parameters are changed

according to hydrolytic damage. More recently, a nonlinear viscoelastic model was used to simulate the time-dependent performance of biodegradable structures (Muliana and Rajagopal, 2012). In that work, the authors considered that hydrolytic damage depends on the deviatoric strain tensor and the concentration of water. Thus, at each time increment step, damage must be calculated in the material point of the continuous model. First water concentration at each material point is updated based on Fick's law. Then the hydrolytic damage is updated as function of the deviatoric strain tensor. Finally, the constitutive relation is updated at each time increment. This method enables to model the relaxation behavior (or creep) during degradation, and it is reasonably good to model moderate deformations. However, in many applications, the mechanical behavior of biodegradable polymers should be analyzed considering large deformation theories (Khan and El-Sayed, 2012). Thus Khan and El-Sayed (2012) developed a phenomenological constitutive viscoelastic-plastic model, which is able to predict the response of biodegradable polymers under large deformations. The model consists of a nonlinear elastic spring element acting in parallel with a variable number of Maxwell elements. The hyperelastic response of both springs in the elastic branch and in the Maxwell branch is governed by the Ogden-type free energy function. The model was based on the phenomenological approach and some of its capabilities, mainly at large deformations, require experimental validation. These types of methods allow the four-dimensional modeling, where the fourth dimension is the degradation time. Yet, the characteristic time of degradation is different from the characteristic viscoelastic time for stress relaxation or creep. If the material has viscoelastic attributes, then the degradation time-dependent phenomenon couples with the time-dependent mechanical behavior of the material. Stretching induces stress relaxation with time by means of viscous flow of the material. Besides, in parallel, stretching induces chemical scissions of the molecules, which provide an additive pathway for relaxation (Khan and El-Sayed, 2012).

The viscoplastic constitutive model used in this work, the Bergström-Boyce model (Bergström and Boyce, 1998) allows simulating the performance of polymers undergoing large deformations. On the other hand, it is a physical inspired polymer model. An important motivation for using physically based constitutive theory to simulate the mechanical behavior of a polymer is that the model can be calibrated through a relative small set of simple mechanical tests, such as uniaxial loading, and enables accurate predictions for other loading cases (Bergström et al., 2002). Together, it enables to simulate the monotonic tests of polymers at different strain rates and it also enables to simulate hysteresis, which occurs under unloading-reloading cycles at different strain levels (Bergström et al., 2002). Unlike the other material models, which were used and adapted to simulate the mechanical behavior during degradation, the Bergström-Boyce model, since it is viscoplastic, enables to simulate the irreversible accumulation of plastic strain. This phenomenon leads dimension instability and consequent design problems. Therefore, in this work, a parametric study is presented for a polymeric blend of PLA-PCL, showing the evolution of the material model parameters during hydrolytic degradation, and analyzing those parameters more sensible to this process. In this investigation, based on experimental results, the limitation and potentialities of the Bergström-Boyce model to simulate a biodegradable polymer over large range deformations under hydrolytic biodegradation are evaluated. Finally, a method is proposed, based on this analysis, to simulate the three-dimensional viscoplastic mechanical behavior during hydrolytic degradation. From the author's knowledge, few methods were developed to predict the mechanical behavior during hydrolytic degradation. These are based on hyperelastic models (Soares *et al.*, 2010; Vieira *et al.*, 2011a), or quasi-linear viscoelastic models (Muliana and Rajagopal, 2012), or phenomenological viscoplastic models (Khan and El-Sayed, 2012). However the calibration and validation of these methods was restricted to moderate deformations. On the other hand, in the present work, a method based on a viscoplastic model, physical inspired on the polymeric microstructure, was calibrated and validated for large deformations.

## 3.  CONSTITUTIVE MODEL

In the constitutive model, the mechanical behavior is decomposed into two parts: an equilibrium response, modeled by a hyperelastic constitutive model (defined as Network A), and a time-dependent deviation from equilibrium, defined by a viscoplastic constitutive model (defined as Network B) as shown by figure 2. In fact the Network B is composed of an elastic element (also modeled by a hyperelastic constitutive model) in series with a time-dependent element, which acts to relieve the strain of the Network A in function of the time. According to the rheological representation of the constitutive model, shown in figure 2, the material is modeled as two polymer networks acting in parallel (Bergström and Boyce, 1998).
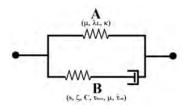


Figure2. Rheological representation of Bergström-Boyce model, adapted from (Bergström and Boyce, 1998)

Finite deformation continuum mechanics requires the specification of reference and deformed configurations. Let X denotes the components of a Cartesian vector specifying a material point in the reference configuration. Then x(X, t) denotes the same material point in the deformed configuration, and represents the motion of this material point. The total deformation gradient is defined by equation 6:

$$F = F_{ij} = \frac{\partial x_i}{\partial X_j} \tag{6}$$

Since deformation in Network A is the same of Network B, then $F=F_A=F_B$. The deformation gradient in Network B can be further decomposed into a plastic deformation followed by an elastic deformation ($F_B=F^e{}_B F^p{}_B$), where the plastic deformation represents the configuration obtained by a complete virtual elastic unloading of Network B to a stress free state. The response of Network A is given by the Arruda-Boyce model (Arruda and Boyce, 1993a), also known as eight-chain model. The Arruda-Boyce eight-chain hyperelastic model is an extension of the neo-Hookean model, which takes non-linear Langevin chain statistics into account when deriving the strain energy density function. The stress response of the eight-chain model is given as:

$$\sigma_A = \frac{\mu}{J\bar{\lambda}^*} \cdot \frac{\mathcal{L}^{-1}(\bar{\lambda}^*/\lambda_L)}{\mathcal{L}^{-1}(1/\lambda_L)} \text{dev}[B^*] + \kappa(J - 1)I \tag{7}$$

where $\mu$ is the shear modulus, $\kappa$ the bulk modulus, and $\lambda_L$ is the limiting chain stretch. I is the second order identity tensor. $\mathcal{L}^{-1}(x)$ is the inverse Langevin function, where $\mathcal{L}(x)=[\coth(x) - 1/x]$, is the Langevin function. According to Gaussian statistics the shear modulus $\mu$ is calculated as $\mu = NbT$, where $N$ is the number of polymer chains per unit volume, $b$ is the Boltzmann constant, and $T$ is temperature (Arruda and Boyce, 1993a). The Jacobian is defined as $J=\det[F]$. $\bar{\lambda}^*$ is the applied chain stretch, which can be calculated from:

$$\bar{\lambda}^* = \sqrt{\frac{\text{tr}B^*}{3}} \tag{8}$$

$B^*=J^{2/3}B= J^{2/3}FF^T$ is the distortional left Cauchy-Green tensor and $\sigma_A$ is the Cauchy stress tensor (also known as true stress tensor) acting in Network A. The stress on Network B is also given by the eight-chain model:

$$\sigma_B = \frac{s\mu}{J_B^e \bar{\lambda}_B^{e*}} \cdot \frac{\mathcal{L}^{-1}(\bar{\lambda}_B^{e*}/\lambda_L)}{\mathcal{L}^{-1}(1/\lambda_L)} \text{dev}[B_B^{e*}] + \kappa(J_B^e - 1)I \tag{9}$$

where $s$ is a dimensionless material parameter, which specifies the shear modulus of Network B relative to Network A, and $\bar{\lambda}_B^{e*}$ is the chain stretch in the elastic part of Network B. Using this representation, the total Cauchy stress tensor $\sigma_= \sigma_A+\sigma_B$. The velocity gradient in Network B, $L_B = \dot{F}_B F_B^{-1}$, and the deformation gradient in Network B can be decomposed into elastic and viscoplastic components ($F_B=F^e{}_B F^p{}_B$). Hence:

$$L_B = \left[\frac{d}{dt}(F_B^e F_B^p)\right](F_B^e F_B^p)^{-1} = \left[\dot{F}_B^e F_B^p + F_B^e \dot{F}_B^p\right](F_B^p)^{-1}(F_B^e)^{-1} =$$
$$= \dot{F}_B^e (F_B^e)^{-1} + F_B^e \dot{F}_B^p (F_B^p)^{-1}(F_B^e)^{-1} = L_B^e + F_B^e L_B^p (F_B^e)^{-1} = L_B^e + \tilde{L}_B^p \tag{10}$$

where the velocity gradient L can be decomposed into the sum of stretch rate and spin tensors, D and W respectively:

$$L_B^p = \dot{F}_B^p (F_B^p)^{-1} = D_B^p + W_B^p \tag{11}$$

$$\tilde{L}_B^p = \tilde{D}_B^p + \tilde{W}_B^p \tag{12}$$

To ensure the unloading unique, the viscous spin tensor is prescribed zero, i.e. $\tilde{W}_B^p \equiv 0$, according to (Bergström and Boyce, 1998; Bergström et al., 2002). The rate of viscoplastic deformation of Network B is constitutively prescribed by:

$$\tilde{L}_B^p = \tilde{D}_B^p = \dot{\gamma}_B N_B = \dot{\gamma}_B \frac{\text{dev}[\sigma_B]}{\tau} = \dot{\gamma}_B \frac{\text{dev}[\sigma_B]}{\|\text{dev}[\sigma_B]\|_F} \tag{13}$$

where $N_B$ gives the direction of the driving stress state of the relaxed configuration and $\dot{\gamma}_B$ is an effective creep rate. $\tau=\|\text{dev}[\sigma_B]\|_F$ is the effective stress, which drives the viscous flow. The time derivative of $F_B^p$ can be derived as follows:

$$\tilde{L}_B^p = F_B^e \dot{F}_B^p (F_B^p)^{-1} (F_B^e)^{-1} = \dot{\gamma}_B N_B \tag{14}$$

and:

$$\dot{F}_B^p = \dot{\gamma}_B (F_B^e)^{-1} \frac{dev[\sigma_B]}{\|dev[\sigma_B]\|_F} F_B^e F_B^p \tag{15}$$

The effective creep rate-equation for viscous flow is given by (Bergström and Boyce, 1998; Bergström *et al.*, 2002):

$$\dot{\gamma}_B = \dot{\gamma}_0 (\overline{\lambda_B^p} - 1 + \xi)^C \left[ R \left( \frac{\tau}{\tau_{base}} - \hat{\tau}_{cut} \right) \right]^m \tag{16}$$

where $\dot{\gamma}_0 = 1$ is a constant introduced to ensure dimensional consistency, $R(x)=[(x + |x|)/2]$ is the ramp function, $\hat{\tau}_{cut}$ is a cut-off stress such that no flow will occur for values lower than the cut-off stress, $\tau_{base}$ represents the flow resistance, *m* is a positive stress exponential, $\xi$ is a strain adjustment factor, *C* is a strain exponential constant, which is restricted at the interval [-1, 0], and (Bergström and Boyce, 1998):

$$\overline{\lambda_B^p} = \sqrt{\frac{tr[F_B^p F_B^{p^T}]}{3}} \tag{17}$$

## 4. MATERIALS AND METHODS

Suture fibers of PLA–PCL (composition 90:10, with 400 μm in diameter) were provided by *Chirmax*. First, non degraded specimens were evaluated. Three test specimens of 100mm long were cut for each experimental set. The distance between the grips was set to 50 mm and, non degraded specimens were monotonically tensile tested in a universal testing machine (TIRAtest 2705), with a load cell of 500 N and grips commonly used in fiber testing, at displacement rates of 500 mm/min and 15 mm/min.

In addition to these monotonic tensile tests, one cyclic test was done using the same setup, with a load displacement rate of 50mm/min and unload displacement rate of 5mm/min. The first cycle was loaded up to 0.7 mm, then reloaded up to 1.5 mm, 3 mm, 4.5 and 6 mm in the 5th cycle. The unloading between each cycle was conducted until reach a stress free state.

Second, the fiber specimens were placed in 50 ml test tubes and submitted to four different degradation steps (0, 2, 4 and 8 weeks) under phosphate buffer solution (PBS) at constant temperature (37 ◦C). A similar monotonic tensile test, at displacement rate of 250 mm/min, was performed on dry specimens (24 h in incubator at 37 ◦C) at the end of each degradation step.

The experimental results, published in previous work (Vieira *et al.*, 2013; Vieira *et al.*, 2011a), exposed the nonlinear time-dependent mechanical behavior of PLA-PCL suture fibers. Based on these results (the average of three tests), the inverse analyses to identify the parameters of the viscoplastic model was done using MCalibration[TM] software (from *Veryst Engineering*). The inverse parameterization technique used to minimize the difference between the experimental results and the model predictions was the Nelder-Mead method, which is implemented in the MCalibration[TM] software. In addition, a parametric study for all the parameters was performed using 3 sets of values (low, mean and high), where the mean corresponds to the value determined by inverse parameterization, and where the low and high values correspond to deviations of more or less 10 percent of the mean value. This parametric study enabled to identify the most sensitive parameters of the material model for the prediction of the experimental results. After that, another inverse parameterization was done where the two active parameters were those most sensitive, while the other parameters were set to averaged values obtained in the previous inverse analyses. After determining the two most sensitive parameters at each degradation step, they were fitted by linear regression as function of the degradation damage *d* model as defined by Vieira *et al.* (2011a). Finally, the predictions using the two most sensitive parameters at each degradation step, calculated by the correspondent linear regression, were compared to the experimental results. It is important to highlight that only the results of monotonic tensile tests at 250 mm/min were used in the analyses to identify the parameters of the viscoplastic model during hydrolytic degradation.

## 5. DISCUSSION OF RESULTS

In the figure 3a) it is possible to observe that the evaluated viscoplastic model was able to simulate the time-dependent nature of the polymer in this range of strain rates. By using these two loading cases in the inverse analyses, the coefficient of determination $R^2$ was very close to 1(one), meaning that the model was able to predict the mechanical behavior of the polymer at different strain rates very accurately.

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In the figure 3b), it is possible to identify that the evaluated viscoplastic model was also able to simulate the hysteric effect commonly observed in polymers. By using cyclic unloading-reloading and monotonic loading cases in the inverse analyses, the coefficient of determination $R^2$ was still very close to 1(one).
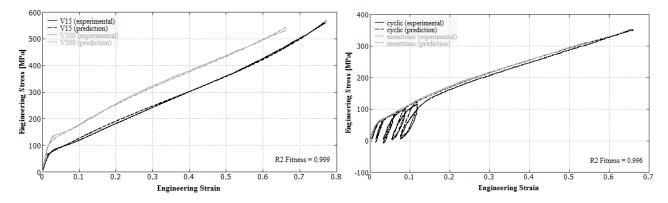


Figure 3. Experimental results of non degraded PLA-PCL fiber, and prediction via viscoplastic Bergström-Boyce model a) monotonic tensile test at two displacement rates (500 and 15mm/min), b) cyclic tensile test

From figures 4 it is possible to see that the evaluated viscoplastic model was also able to simulate the non-linear mechanical behavior until rupture in monotonic tensile test at different hydrolytic degradation steps, with the coefficient of determination $R^2$ always above 0.995. Although precision is slightly reduced with hydrolytic degradation time. Comparing to hyperelastic models such as the Neo-Hookean or the Arruda-Boyce models, the coefficient of determination $R^2$ does not reach 0.98, and reduces considerably during the hydrolytic degradation time ($R^2$ does not reach 0.8 after 8 weeks of hydrolytic degradation). Thus, the coefficient of determination is much higher for the Bergström-Boyce models (after 8 weeks of hydrolytic degradation $R^2$ is 0.995).
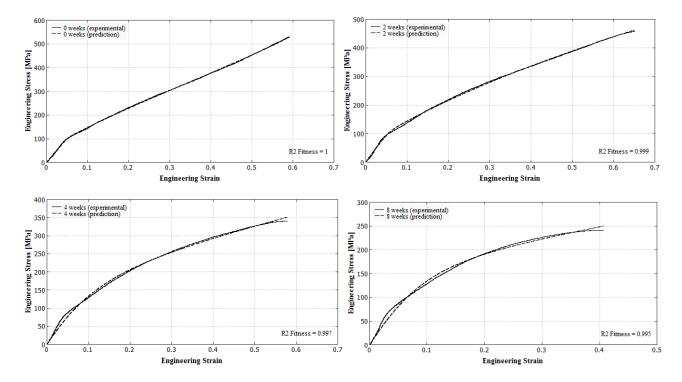


Figure 4. Experimental results of monotic tensile test at 250 mm/min of PLA-PCL fiber, and prediction via viscoplastic Bergström-Boyce model, after 0, 2, 4 and 8 weeks of hydrolytic degradation

In the table 1, a list of the material model parameters, which are used on the predictions of the mechanical behavior during hydrolytic degradation, are presented at each degradation step. Based on the parametric study, it is concluded that the shear modulus $\mu$ is the most sensitive parameter of the Bergström-Boyce model, for all the hydrolytic degradation steps. The locking stretch $\lambda_L$ is another sensitive parameter, which was studied. We verify that deviations from the determined value affect the prediction, mainly at higher stress levels. However, since the hydrolytic degraded

specimens break at lower stress levels, this parameter becomes almost insensitive in the predictions of the mechanical behavior of the polymer after two weeks of hydrolytic degradation and forward. Also the flow resistance $\tau_{base}$ is sensitive to deviations. Although it is much less sensitive than the shear modulus $\mu$, it is observed great changes of its value during the degradation process. On the other hand, stress exponential $m$ is also sensitive to deviations, but its value remains in the same order of magnitude. The strain exponential $C$ is nearly insensitive for values close to zero. The correlation with experimental results decreases for values close to -1 (minus one). This same trend was observed by Bergström et al. (2002), in the case o UHMWPE, where the optimal value of the material parameter $C$ was very close to zero. However, for elastomeric materials, the same parameter C has a value close to -1 (minus one) (Bergström and Boyce, 1998). Hence the magnitude of the plastic flow rate is nearly independent on the strain level.

Table 1. List of the model parameters determined by inverse parameterization at each hydrolytic degradation step

| Model parameters | 0 weeks | 2 weeks | 4 weeks | 8 weeks |
|---|---|---|---|---|
| $\mu$ - Shear modulus of network A | 355.439 | 331.842 | 256.811 | 192.686 |
| $\lambda_L$ - Locking stretch | 1.55813 | 5.18064 | 9.99997 | 5.42087 |
| $\kappa$ - Bulk modulus | 59137.1 | 52603.8 | 2522.86 | 10961.5 |
| $s$ - Relative stiffness of network B | 0.994461 | 1.03951 | 1.40451 | 2.27284 |
| $\xi$ - Strain adjustment factor | 0.286773 | 0.189326 | 0.500236 | 0.482787 |
| $C$ - Strain exponential | -0.48398 | -0.54034 | -0.00815 | -1.8e-08 |
| $\tau_{base}$ - Flow resistance | 48.2916 | 94.9219 | 1645.91 | 1402.44 |
| $m$ - Stress exponential | 13.4184 | 5.68314 | 1.1001 | 1.34039 |
| $\hat{\tau}_{cut}$ - Normalized cut-off stress for flow | 0.008102 | 0.009484 | 4.17e-06 | 0.003313 |

Based on these observations, it was performed another inverse analysis, considering only these two variable parameters: the shear modulus $\mu$ and the flow resistance $\tau_{base}$. The other parameters were set constant during the hydrolytic degradation process, assuming averaged values determined from the different hydrolytic degradation steps, which were calculated in the previous inverse analyses. The parameters determined by this way are shown in table 2. As it can be seen, the material was assumed to be nearly incompressible, since the bulk modulus $\kappa$ used, which represents the resistance to volume changes, is very high from the beginning of the hydrolytic degradation process until eight weeks. Furthermore, using higher values of shear modulus will have a negligible effect on the prediction, while a small value will decrease the correlation between the prediction and the experimental results. It was observed that the shear modulus decreases nearly linear with the hydrolytic damage. This same trend was also reported in a previous work (Vieira et al., 2011a), where the neo-Hookean, Mooney-Rivlin and second reduced hyperelastic models were used to predict the mechanical behavior of the same biodegradable polymer. Muliana and Rajagopal (20012) also assumed in their own viscoelastic model that shear modulus decreases with hydrolytic degradation, i.e. hydrolytic degradation softens the polymers. On the order hand, Soares (2008) reported that the material becomes less viscous during hydrolytic degradation, and returns faster to an equilibrium state. This assumption is also consistent to the results of this work, where the flow resistance $\tau_{base}$ increases nearly linear with the hydrolytic damage. This may be explained by the reduction of the mobility of the polymer chains during hydrolytic degradation, which becomes more brittle and resistant to flow.

Table 2 List of the material model parameters determined by inverse parameterization at each hydrolytic degradation step, with only two active parameters (the shear modulus $\mu$ and the flow resistance $\tau_{base}$)

| Model parameters | 0 weeks | 2 weeks | 4 weeks | 8 weeks |
|---|---|---|---|---|
| $\mu$ - Shear modulus of network A | 408.062 | 335.217 | 261.177 | 211.162 |
| $\lambda_L$ - Locking stretch | 5 | 5 | 5 | 5 |
| $\kappa$ - Bulk modulus | 30000 | 30000 | 30000 | 30000 |
| $s$ - Relative stiffness of network B | 1.5 | 1.5 | 1.5 | 1.5 |
| $\xi$ - Strain adjustment factor | 0.4 | 0.4 | 0.4 | 0.4 |
| $C$ - Strain exponential | -0.25 | -0.25 | -0.25 | -0.25 |
| $\tau_{base}$ - Flow resistance | 32.109 | 139.271 | 209.505 | 287.162 |
| $m$ - Stress exponential | 3 | 3 | 3 | 3 |
| $\hat{\tau}_{cut}$ - Normalized cut-off stress for flow | 0.005 | 0.005 | 0.005 | 0.005 |

The linear fitting of these two parameters (the shear modulus $\mu$ and the flow resistance $\tau_{base}$) as function of the hydrolytic damage $d$ is shown in the figure 5. A good correlation of the linear fitting was demonstrated, with the coefficient of determination $R^2$ above 0.97 for both parameters. Based on these linear equations, the shear modulus $\mu(d)$ and the flow resistance $\tau_{base}(d)$ were calculated, and they are shown in table 3.
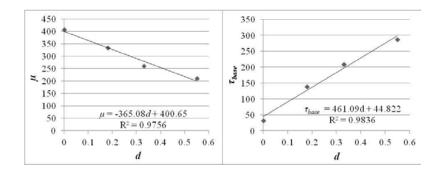
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Reliability in ecodesign of interior parts in aerospace and automobile industry using biodegrable thermoplastics



Figure 5. Evolution of the material parameters of the Bergtröm-Boyce model, shear modulus $\mu$ and flow resistance $\tau_{base}$, during hydrolytic degradation

Table 3 List of the shear modulus $\mu$ and the flow resistance $\tau_{base}$ used at each hydrolytic degradation step, determined by the linear fitting equation as function of hydrolytic damage

| Model parameters | 0 weeks | 2 weeks | 4 weeks | 8 weeks |
|---|---|---|---|---|
| $\mu$ - Shear modulus of network A | 400.65 | 334.936 | 280.174 | 199.856 |
| $\tau_{base}$ - Flow resistance | 44.822 | 127.818 | 196.982 | 298.422 |

Then these values were used together with the other material model parameters values previously assumed constant during hydrolytic degradation, to predict the mechanical behavior of the polymer during hydrolytic degradation. The basic assumption in this formulation consists on the introduction of the hydrolytic damage scalar field, which does not change the nature of the constitutive law, and the model still exhibits viscoplastic constitutive behavior at any hydrolytic degradation step. A comparison of these predictions against the experimental monotonic tensile test results, at different hydrolytic degradation steps is shown in figure 6. Although the result of these predictions, using the proposed method to estimate the material model parameters, is less accurate than the initial predictions, using the inverse analyses of all the parameters, the result has still a satisfactory correlation, with the coefficient of determination $R^2$ above 0.98. However, based on this method, two of the parameters are functions of the hydrolytic damage $d$, while the other parameters remain constant during hydrolytic degradation.
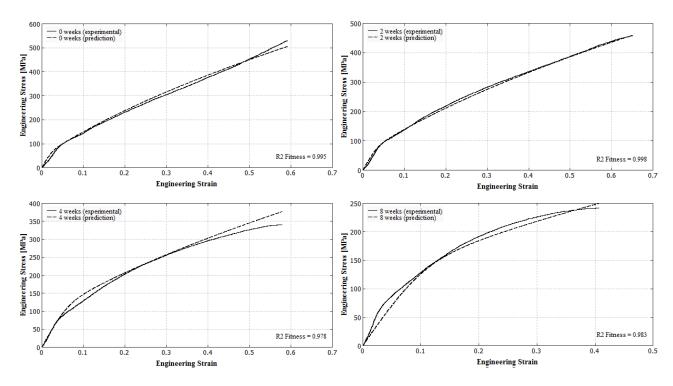


Figure 6. Experimental results of monotic tensile test at 250 mm/min of PLA-PCL fiber, and prediction via viscoplastic Bergström-Boyce model, after two weeks of hydrolytic degradation

## 6. CONCLUSIONS

Biodegradable polymers, as conventional polymers are known by their non-linear and time-dependent mechanical behavior. The method presented in this work is the first one based on a viscoplastic constitutive model validated experimentally for large deformations. Although the application of this method was only demonstrated, in the present work, for this particular blend, the authors had evaluated the method for other biodegradable polymers, such PDO and PGA. Furthermore, this can still be extended to other thermoplastic biodegradable materials, since the Bergström-Boyce model was originally developed for engineering rubbers, but was also used to predict the mechanical behavior of other thermoplastics and other soft materials with both non-linear and time-dependent mechanical behavior. Although this model is much more complex than the hyperelastic models usually used to model the mechanical behavior of biodegradable polymer, it enables to simulate realistic loading cases usually similar to those in service. These in service loading cases comprise loading at various rates, and cyclic loading above yielding. Hence, the investigated material model is able to capture the more significant phenomena, which occur in biodegradable polymers, such as relaxation and creep, hysteresis and plastic strain accumulation with hydrolytic biodegradation. In fact, this could be confirmed using the proposed method to predict the mechanical behavior of biodegradable polymers based on the Bergtröm-Boyce constitutive model. For this method, the shear modulus $\mu$ and the flow resistance $\tau_{base}$ are linear functions of the hydrolytic damage, while the other material model parameters remain constant during the hydrolytic degradation process. Therefore, the proposed method is an important tool to be used in the design and dimensioning of biodegradable devices according to mechanical and durability requirements.

The present investigation can be further updated to more detailed models, which consider the hydrolytic degradation rate dependence on temperature, environment and stress state. In these more complicated problems, hydrolytic damage will depend not only on the biodegradation time, but also on the water concentration and the hydrolysis kinetic constant; no longer constants but now time, geometry, biodegradation media, temperature and stress state dependent. In these cases, hydrolytic damage will be a local internal variable, which varies along the volume and must be calculated previously at each material point and at each biodegradation step. However, the proposed adaptation of the studied constitutive model is still valid from there forward.

## 7. ACKNOWLEDGEMENTS

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