

## CONSIDERATIONS FOR THE DESIGN OF BIODEGRADABLE DEVICES

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**Abstract.** Several biodegradable polymers are used in many products with short life cycle. Aliphatic polyesters, such as polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL), polydioxone (PDO) and others, have been commonly used in biodegradable products. Important applications of these are found in the biomedical field, where biodegradable materials are applied on manufacturing scaffolds that temporarily replace the biomechanical functions of a biologic tissue, while it progressively regenerates its capacities. In the case of commodity products, biodegradable plastics claim clear environmental advantages in several brief use applications, mainly in their final stage of life (waste disposal), which can clearly be evident through life cycle assessment. Performance of a device depends of its behavior to a mechanical, thermal or chemical applied stress. It is mostly conditioned by the materials selection and dimensioning of the product. For a biodegradable product, performance will decrease along its degradation. From the final user point of view, performance should be enough for the predicted use, during all its life cycle. Biodegradable plastics can present short term performances similar to conventional plastics. Hydrolytic and/or enzymatic chain cleavage of these materials leads to  $\alpha$ -hydroxyacids, which, in most cases, are ultimately assimilated in human body or in a composting environment. However, each of these has some shortcomings, in terms of mechanical properties and degradation time, which restrict their applications. The combination of these materials, by copolymerization or blending, or using a composite solution of several materials with different degradation rates, enables a range of mechanical properties and degradation rates. These approaches can improve or tune the original properties of the polymers. The mechanical behaviour of biodegradable materials along its degradation time, which is an important aspect of the project, is still an unexplored subject. The failure criteria for maximum strength as a function of degradation time have traditionally been modeled according to a first order kinetics. In this work, hyper elastic constitutive models, such as the Neo-Hookean, the Mooney-Rivlin modified and the second reduced order will also be discussed. An example of these is shown for a blend composed of polylactic acid (PLA) and polycaprolactone (PCL). A numerical approach using ABAQUS is presented, where the material properties of the model proposal are automatically updated in correspondence to the degradation time, by means of a User Material subroutine (UMAT). The parameterization of the material model proposal for different degradation times were achieved by fitting the theoretical curves with the experimental data of tensile tests made on PLA-PCL blend (90:10). The material model proposal presented here could be used as a design toll for generic biodegradable devices.

**Keywords:** biodegradable, materials, selection, dimensioning, design

### 1. INTRODUCTION

There are many biodegradable polymers commercially available to produce a great variety of plastic products, each of them with suitable properties according to the application. However the design process is slight more complex. It must contemplate besides the mechanical stress degradation, also defined as the time-dependent cumulative irreversible damage, such as fatigue or creep damage, the degradation due to hydrolysis. In this work, important considerations will be elucidated about biodegradable product design, in the phase of material selection and dimensioning.

Biodegradable polymers can be classified as either naturally derived polymers or synthetic polymers. A large range of mechanical properties and degradation rates are possible among these polymers, for many applications in briefly used products. 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. 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), polyhydroxyalkanoates (PHA's) and polyethylene oxide (PEO) among others. They can be processed as other thermoplastic materials.

The poly- $\alpha$ -hydroxyesters, PLA, PGA and their copolymers are the most popular aliphatic polyesters that have been synthesized for more than 30 years. The left-handed (L- lactide) and right-handed (D-lactide) are the two enantiometric forms of PLA, with PDLA having a much higher degradation rate than PLLA. An intensive overview was done by

Auras *et al.* (2004). PLLA is a rather brittle polymer with a low degradation rate, and compounding with PCL is frequently employed to improve mechanical properties. PCL is also hydrophobic with a low degradation rate, much more ductile than PLA (Södergard and Stolt, 2002). PGA, since it is a hydrophilic material presents a high degradation rate. The combination of PGA with PLA is usually employed to tune degradation rate (Nair and Laurencin, 2007). Polyhydroxyalkanoates (PHA's) is the largest class of aliphatic polyesters, comprising poly 3-hydroxybutyrate (PHB), copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV), poly 4-hydroxybutyrate (P4HB), copolymers of 3-hydroxybutyrate and 3-hydroxyhexanoate (PHBHHx) and poly 3-hydroxyoctanoate (PHO) and its blends. The changing PHA compositions also allow favourable mechanical properties and degradation times within desirable time frames (Chen and Wu, 2005). Natural polymers used in biodegradable products include starch, collagen, silk, alginate, agarose, chitosan, fibrin, cellulosic, hyaluronic acid-based materials, among others. In table 1, some physical properties are presented for different aliphatic polyesters.

Table 1. Material properties of biodegradable thermoplastics: Tm, melting temperature; Tg, glass transition temperature; Mw, number average molecular weight; Young Modulus; Tensile Strength and Maximum Elongation.

Material	Tg (°C)	Tm (°C)	Mw (g/mol)	Young Modulus (MPa)	Tensile Strength (MPa)	Maximum Elongation (%)	References
PLA	62	138					(Agarwal <i>et al.</i> , 1998)
				3400	60		(Oksmana <i>et al.</i> , 2003)
	59		3.34x10 <sup>5</sup>				(Navarro <i>et al.</i> , 2005)
	45-60	150-162		350-3500	21-60	2.5-6	(Van de Velde <i>et al.</i> , 2002)
				3300	57.8		(Yew <i>et al.</i> , 2005)
PLLA			4.5x10 <sup>5</sup>				(Zhang <i>et al.</i> , 2007)
	53	170-180					(Mohantya <i>et al.</i> , 2000)
	65	175	1.1x10 <sup>5</sup>	3200-3700	55-60		(Zuideveld <i>et al.</i> , 2006)
	55-65	170-200		2700-4140	15.5-150	3-10	(Van de Velde <i>et al.</i> , 2002)
PGA					37		(Ashammakhi <i>et al.</i> , 1995)
	35-45	220-233		6000-7000	60-100	1.5-20	(Van de Velde <i>et al.</i> , 2002)
PDO			1.5x10 <sup>5</sup>		139	62	(Hong <i>et al.</i> , 2006)
PDLLA			3.25x10 <sup>5</sup>				(Tsuji and Ikada, 1996)
	51,6			2800	26	11.4	(Chen <i>et al.</i> , 2003)
	50-60			1000-3450	27.6-50	2-10	(Van de Velde <i>et al.</i> , 2002)
PDLGA			1.2x10 <sup>5</sup>				(Zilberman, 2007)
PCL	-60		2.7x10 <sup>5</sup>				(Tsuji and Ikada, 1996)
		53.1	2.7x10 <sup>4</sup>				(Chen <i>et al.</i> , 2003)
	-60--65	58-65		210-440	20.7-42	300-1000	(Van de Velde <i>et al.</i> , 2002)
	-60	60	1.2x10 <sup>5</sup>				(Todo <i>et al.</i> , 2007)
PDLA-PGA	40-60			1000-4340	41.4-55.2	2-10	(Van de Velde <i>et al.</i> , 2002)
PGA-PCL			1.5x10 <sup>5</sup>		192.1	55	(Hong <i>et al.</i> , 2006)
PEO			3x10 <sup>5</sup>				(Fan <i>et al.</i> , 2003)
			10 <sup>5</sup> -8x10 <sup>6</sup>	390			(Ferretti <i>et al.</i> , 2005)
	-64						(Nagarajan <i>et al.</i> , 1998)
PHB	5-15	168-182		3500-4000	40	5-8	(Van de Velde <i>et al.</i> , 2002)
PELA				14	26-31		(Cohn <i>et al.</i> , 2005)
PESu	-11.5	104					(Bikiaris <i>et al.</i> , 2006)
PPSu	-35	44					(Bikiaris <i>et al.</i> , 2006)
PBSu	-44	103					(Bikiaris <i>et al.</i> , 2006)

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 device design. But such studies represent a costly

method of iterating the device dimensioning. The mechanical behaviour of biodegradable materials along its degradation time, which is an important aspect of the project, is still an unexplored subject. The failure criteria for maximum strength as a function of degradation time have traditionally been modeled according to a first order kinetics. Many examples of this kind of design challenge can be found in the medical field, ranging from biodegradable sutures (Laufman and Rubel, 1977), pins and screws for orthopedic surgery (Pietrzak *et al.*, 1997), local drug delivery devices (Langer, 1998), tissue engineering scaffolds (Levenberg and Langer, 2004), biodegradable ligaments (Vieira *et al.*, 2009), biodegradable endovascular (Colombo and Karvouni, 2000) and urethral stents (Tabela and Talja, 2003).

In this work, hyper elastic constitutive models, such as the Neo-Hookean, the Mooney-Rivlin modified and the second reduced order will also be discussed. An example of these is shown for a blend composed of polylactic acid (PLA) and polycaprolactone (PCL). A numerical approach using ABAQUS is presented, where the material properties of the model proposal are automatically updated in correspondence to the degradation time, by means of a User Material subroutine (UMAT). The parameterization of the material model proposal for different degradation times were achieved by fitting the theoretical curves with the experimental data of tensile tests made on PLA-PCL blend (90:10). The material model proposal presented here could be used as a design toll for generic biodegradable devices.

## 2. DEGRADATION AND EROSION

All biodegradable polymers contain hydrolysable or oxydable bonds. This makes the material sensitive to moisture, heat, light and also mechanical stress. These different types of polymer degradation (photo, thermal, mechanical and chemical degradation) can be present alone or combined, working synergistically to the degradation. Usually the most important degradation mechanism of biodegradable polymers is chemical degradation via hydrolysis or enzyme-catalysed hydrolysis (Göpferich, 1996). Hydrolysis rates are affected by the temperature or mechanical stress, molecular structure, ester group density as well as by the degradation media used. The crystalline degree may be a crucial factor, since enzymes attack mainly the amorphous domains of a polymer. 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. But while the degree of erosion is estimated from the mass loss, or CO<sub>2</sub> conversion, the degree of degradation can be estimated by measuring the evolution of molecular weight (by size exclusion chromatography [SEC] or gel permeation chromatography [GPC], or the tensile strength evolution (by universal tensile test). So the hydrolytic degradation process is included on the erosion process.

The erosion process can be described by phenomenological diffusion-reaction mechanisms presented in Fig. 1. An aqueous media diffuses into the polymeric material while oligomeric products diffuse outwards to be then bioassimilated by the host environment. Then we have material erosion with correspondent mass loss. On the other hand, degradation refers to mechanical damage and depends on hydrolysis. Within the polymeric matrix, hydrolytic reactions take place, mediated by water and/or enzymes. While water diffuses rapidly well inside the material, enzymes are unable to do it, and so they degrade at surface.

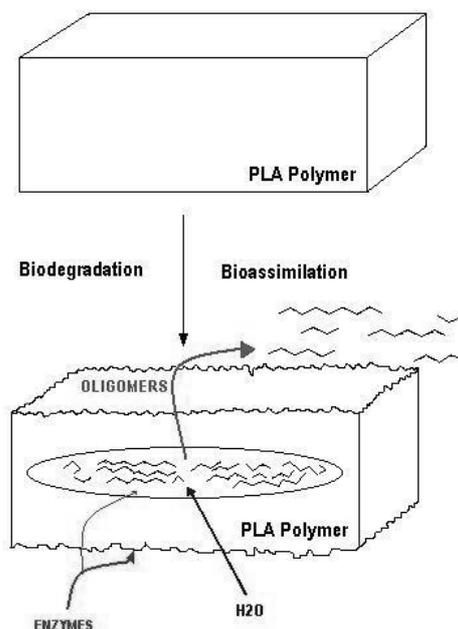


Figure 1. Scheme of erosion process (Vieira, 2010)

## 2.1. Diffusion

After immersion of a biodegradable polymeric device in an aqueous medium, the very first event which occurs is water uptake, up to a saturation of water concentration that depends on the hydrophilicity of the polymer, its crystalline degree and the temperature, pH and flow of the media. The penetrating water rapidly creates a negative gradient of water concentrations from the surface to the centre as expected from a pure diffusion viewpoint. However, this gradient vanishes in a couple of days, when the specimen saturates. Diffusion of small molecules like water is rather fast as compared with degradation. Therefore, one can consider that hydrolysis of ester bonds starts homogeneously along the volume from the beginning. Water uptake can also lead to further recrystallization of the polymer. Water acts as a plasticizer, lowering the glass transition temperature and softening the material.

The water concentration ( $w$ ) along the thickness, and during incubation, is determined using Fick's equation, presented for 1D:

$$\frac{dw}{dt} = D \frac{\partial^2 w}{\partial x^2} \quad (1)$$

or for 3D:

$$\frac{dw}{dt} = D_1 \frac{\partial^2 w}{\partial x^2} + D_2 \frac{\partial^2 w}{\partial y^2} + D_3 \frac{\partial^2 w}{\partial z^2} \quad (2)$$

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

## 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 this scissions occur at the ester groups. A general consequence of such a process is the lowering of the plastic flow ability of the polymer, thus causing the change of a ductile, tough behavior into a brittle one. If the behavior was initially brittle, we will assist an increase in the brittleness. In Fig. 2 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. So, the number of carboxylic end groups will increase with degradation time, while the molecules are being splitted by hydrolysis.

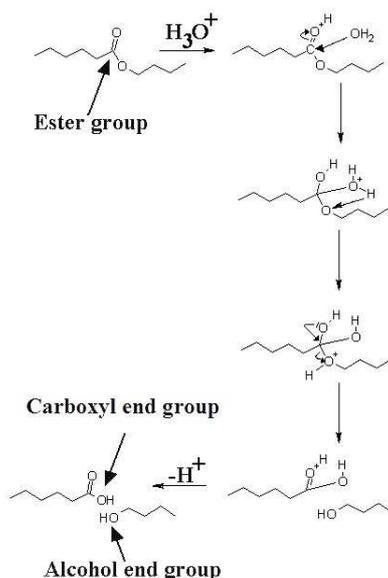


Figure 2. Acid catalyzed hydrolysis mechanism (Vieira *et al.*, 2010)

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 describes the hydrolytic process relative to the carboxyl end groups ( $C$ ), ester concentration ( $E$ ) and water concentration ( $w$ ):

$$\frac{dC}{dt} = kEwC = uC \quad (3)$$

where  $u$  is the medium hydrolysis rate of the material,  $k$  is the hydrolysis rate constant  $E$  and  $w$  are constant in the early stages of the reaction. In addition, water is spread out uniformly in the sample volume (no diffusion control). Using the molecular weight, and since the concentrations of carboxyl end groups are given by  $C=1/M_n$ ; the equation 3 becomes:

$$M_{n_t} = M_{n_0} e^{-ut} \quad (4)$$

where  $M_{n_t}$  and  $M_{n_0}$  are the number-average molecular weight, at a given time  $t$  and initially at  $t=0$ , respectively. This equation leads to a relationship  $Mn = f(t)$ . However, in the design phase of a biodegradable device, it is important to predict the evolution of mechanical properties like tensile strength, instead of molecular weight. It has been shown by Vieira *et al.* (2010) that the fracture strength follows the same trend as the molecular weight:

$$\sigma_t = \sigma_0 e^{-ut} \quad (5)$$

The hydrolytic damage can be written, as Vieira *et al.* (2010), in the form:

$$d_h = 1 - \frac{\sigma}{\sigma_0} = 1 - e^{-ut} = 1 - e^{-kEwt} \quad (6)$$

So the hydrolytic damage depends on the hydrolysis kinetic constant,  $k$ , the concentrations of ester groups,  $E$ , the water concentration in the polymer matrix,  $w$ , and the degradation time. In this example, of homogeneous degradation with instant diffusion, the degradation rate,  $u$ , is constant, and damage only depends on degradation time. Although these considerations are valid in the majority of the cases, in some cases the degradation rate cannot be considered constant.

### 2.3. Surface vs. Bulk erosion

Different types of erosion are illustrated in figure 3. One is homogeneous or bulk erosion without autocatalysis (Fig. 3 c), considered until now, where diffusion is considered to occur instantaneously. Hence, the decrease in molecular weight, the reduction in mechanical properties, and the loss of mass occur simultaneously throughout the entire specimen. One other type is heterogeneous or surface erosion (figure 3 a), in which hydrolysis occurs in the region near the surface, whereas the bulk material is only slightly or not hydrolyzed at all. As the surface is eroded and removed, the hydrolysis front moves through the material core. In this case, in which diffusion is very slow compared to hydrolysis, one must use equation 1 to calculate water concentration  $w(t, x)$  at any instant  $t$  through the thickness  $x$ , before using equations 4 and 5. Surface eroding polymers have a greater ability to achieve zero-order release kinetics, and are therefore ideal candidates for developing devices able to deliver substances such as drugs, aroma, fertilizers, etc (Nair and Laurencin, 2007). Also enzymatic erosion fits on this last type of erosion, since enzymes are unable to diffuse and present a raised hydrolysis kinetic constant  $k$ .

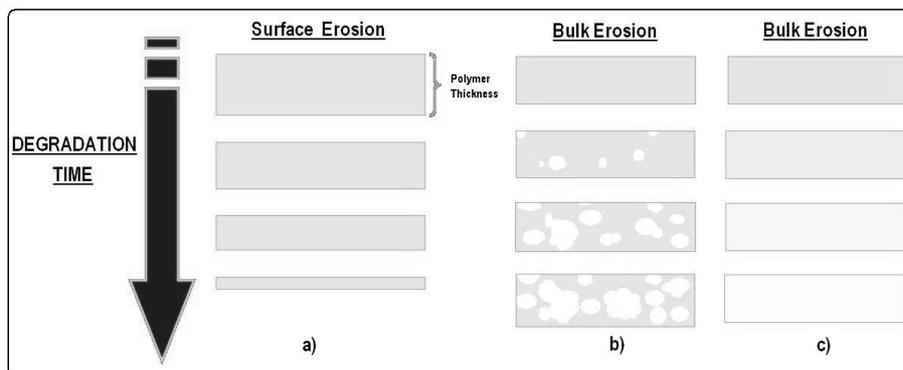


Figure 3. Schematic illustration of three types of erosion phenomenon: (a) surface erosion, (b) bulk erosion with autocatalysis, (c) bulk erosion without autocatalysis (Vieira *et al.*, 2010)

Surface and bulk erosion are ideal cases to which most polymers cannot be unequivocally assigned. We can define the characteristic time of hydrolysis, as the inverse of degradation rate:

$$\tau_H = \frac{1}{kEW} = \frac{1}{u_m} \quad (7)$$

If  $D$  is the diffusion coefficient of water in the polymer and  $L$  is the sample thickness, we can define a characteristic time of diffusion,  $\tau_D$ :

$$\tau_D = \frac{L^2}{D} \quad (8)$$

When  $\tau_H \gg \tau_D$ , water reaches the core of the material before it reacts, and the degradation starts homogeneously. When  $\tau_H \ll \tau_D$ , water reacts totally in the superficial layer and will never reach the core of the material. The degradation starts heterogeneously through the volume. In these cases, a higher surface to volume ratio induces a faster degradation. Another factor that complicates the erosion of biodegradables consists on the hydrolysis reaction is autocatalytic (Siparsky *et al.*, 1998). For example, a thick plate of PLA erodes faster than a thinner one made of the same polymer (Grizzi *et al.*, 1995). This occurs due to retention of the oligomeric hydrolysis products within the material, which are carboxylic acids, causing a local decrease in pH and therefore accelerating the degradation (Göpferich, 1996). As can be seen in figure 3 b), hollow structures are formed as a consequence (Grizzi *et al.*, 1995).

### 3. CONSTITUTIVE MODELS FOR BIODEGRADABLE MATERIALS

A constitutive model for a mechanical analysis is a relationship between the response of a body (for example, strain) and the stress due to the forces acting on this body. A wide variety of material behaviors are described with a few different classes of constitutive equations. Due to the nonlinear nature of the stress vs. strain plot, the classical linear elastic model is clearly not valid for large deformations. Hence, given the nature of biodegradable plastic, classical models such as the neo-Hookean and Mooney-Rivlin models for incompressible hyperelastic materials may be used to describe its mechanical behavior until rupture. For these materials, stiffness depends on the fiber stretch. Mechanical properties of elastomeric materials are usually represented in terms of a strain energy density function  $W$ , which is a scalar function of the deformation gradient.  $W$  can also be represented as a function of the right Cauchy–Green deformation tensor invariants. In general, the strain energy density for an isotropic, incompressible, hyperelastic material is determined by two invariants. The first and second invariants in uniaxial tension are given by:

$$I_C = \lambda^2 + \frac{2}{\lambda} \quad (9)$$

$$II_C = \frac{1}{\lambda^2} + 2\lambda \quad (10)$$

where  $\lambda$  is the axial stretch ( $\lambda=1+\varepsilon$ ), that satisfies  $\lambda \geq 1$ . The neo-Hookean incompressible hyperelastic solid is given a stored energy function of the form:

$$W = \frac{\mu_1}{2}(I_C - 3) \quad (11)$$

where  $\mu_1 > 0$  is the material property, usually called the shear modulus. An extension of this model is the Mooney-Rivlin incompressible hyperelastic solid, which stored energy function has the form:

$$W = \frac{\mu_1}{2}(I_C - 3) + \frac{\mu_2}{2}(II_C - 3) \quad (12)$$

with two material properties  $\mu_1$  and  $\mu_2$ . Higher order stored energy functions may be considered to describe the experimental data, such as a reduced 2<sup>nd</sup> order stored energy function, that includes a mixed term with both invariants of the right Cauchy–Green stretch tensor and an extra material constant  $\mu_3$ , which stored energy function has the form:

$$W = \frac{\mu_1}{2}(I_C - 3) + \frac{\mu_2}{2}(II_C - 3) + \frac{\mu_3}{6}(I_C - 3)(II_C - 3) \quad (13)$$

The axial nominal stress for the three models, neo-Hookean ( $\sigma^{NH}$ ), Mooney-Rivlin ( $\sigma^{MR}$ ) and reduced second order ( $\sigma^{2^{nd} red}$ ), will be given by:

$$\sigma^{NH} = \mu_1 \left( \lambda - \frac{1}{\lambda^2} \right) \quad (14)$$

$$\sigma^{MR} = \mu_1 \left( \lambda - \frac{1}{\lambda^2} \right) + \mu_2 \left( 1 - \frac{1}{\lambda^3} \right) \quad (15)$$

$$\sigma^{2^{nd} red} = (\mu_1 - \mu_3) \left( \lambda - \frac{1}{\lambda^2} \right) + (\mu_2 - \mu_3) \left( 1 - \frac{1}{\lambda^3} \right) + \mu_3 \left( \lambda^2 - \frac{1}{\lambda^4} \right) \quad (16)$$

According to Soares *et al.* (2010) the model constitutive material parameters depend on degradation time. The material parameters are considered to be material functions of degradation damage instead of material constants. Later, Vieira *et al.* (2010) determined that only the first material parameter  $\mu_1$ , vary linearly with hydrolytic damage (as defined in Eq. 6). In this work, a blend of PLA-PCL (90:10) was used. From Fig. 4, one can see that the hyperelastic material models fit well the measured storage energy, for all the degradation steps up to 8 weeks. The experimental data of storage energy was calculated by measuring the area (i.e., by taking the integral) underneath the stress-strain curve, from zero until a certain level of stretch. The neo-Hookean model was the less precise. However it respects the 2<sup>nd</sup> law of thermodynamics where every material parameters  $\mu_i$  must have a positive value. The material parameters were calculated by inverse parameterization of the models with the experimental data, and are listed in table 2.

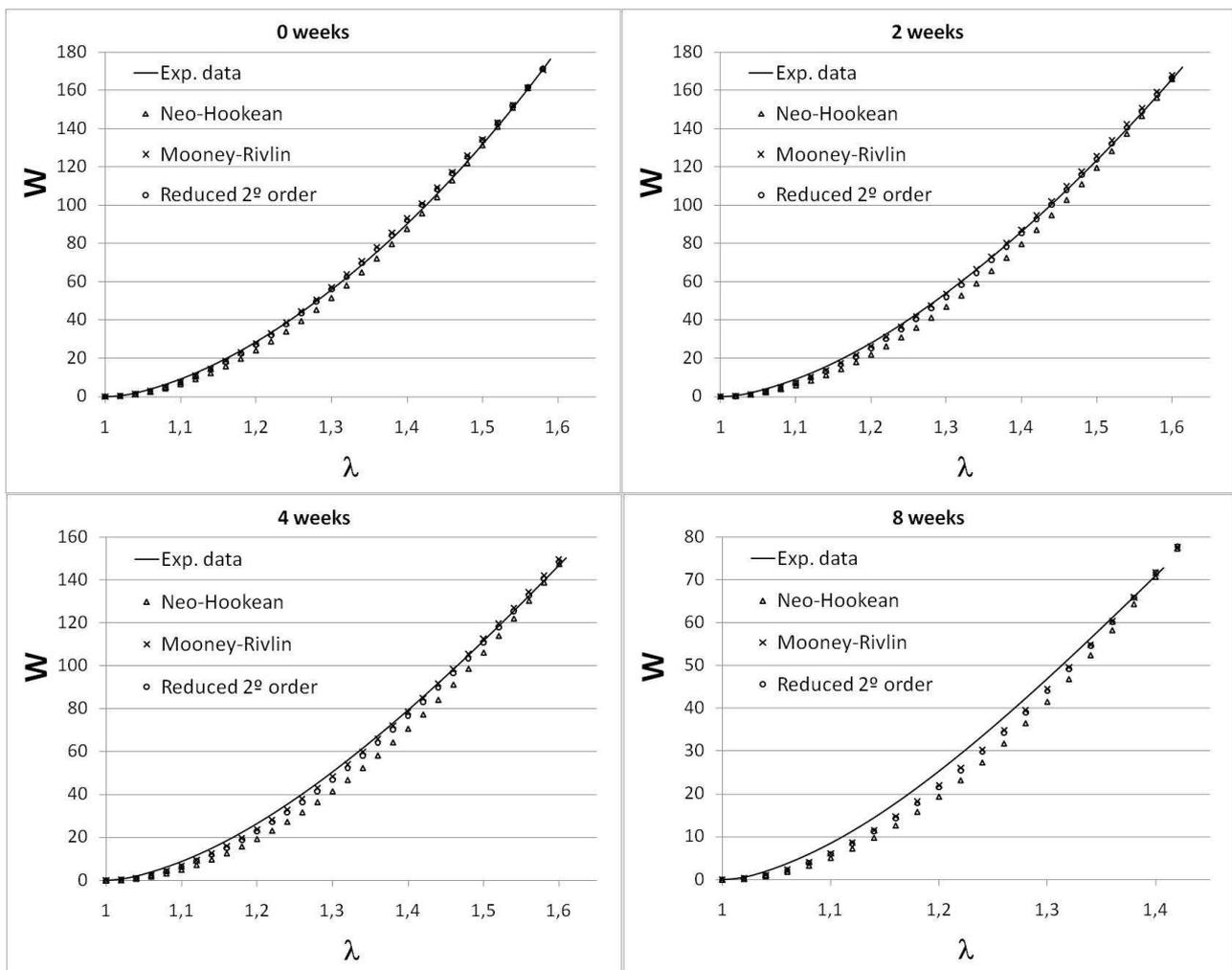


Figure 4. Storage energy vs. axial stretch for 0, 2, 4 and 8 weeks of degradation (Vieira *et al.*, 2010)

From Fig. 6, one can see that the hyper elastic material models allowed a reasonable approximation of the tensile test results. The presented method, that consists on changing the first material parameter with hydrolytic damage,  $\mu_1(d)$ , according to the linear regression (see Fig. 5), enables to describe the mechanical behavior evolution by using equations 14, 15 or 16, while the limit stress is defined by equation 5.

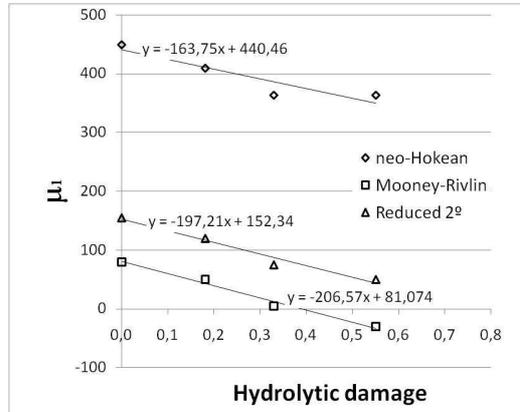


Figure 5. Evolution of the material parameter,  $\mu_1$ , of the models during degradation (Vieira *et al.*, 2010)

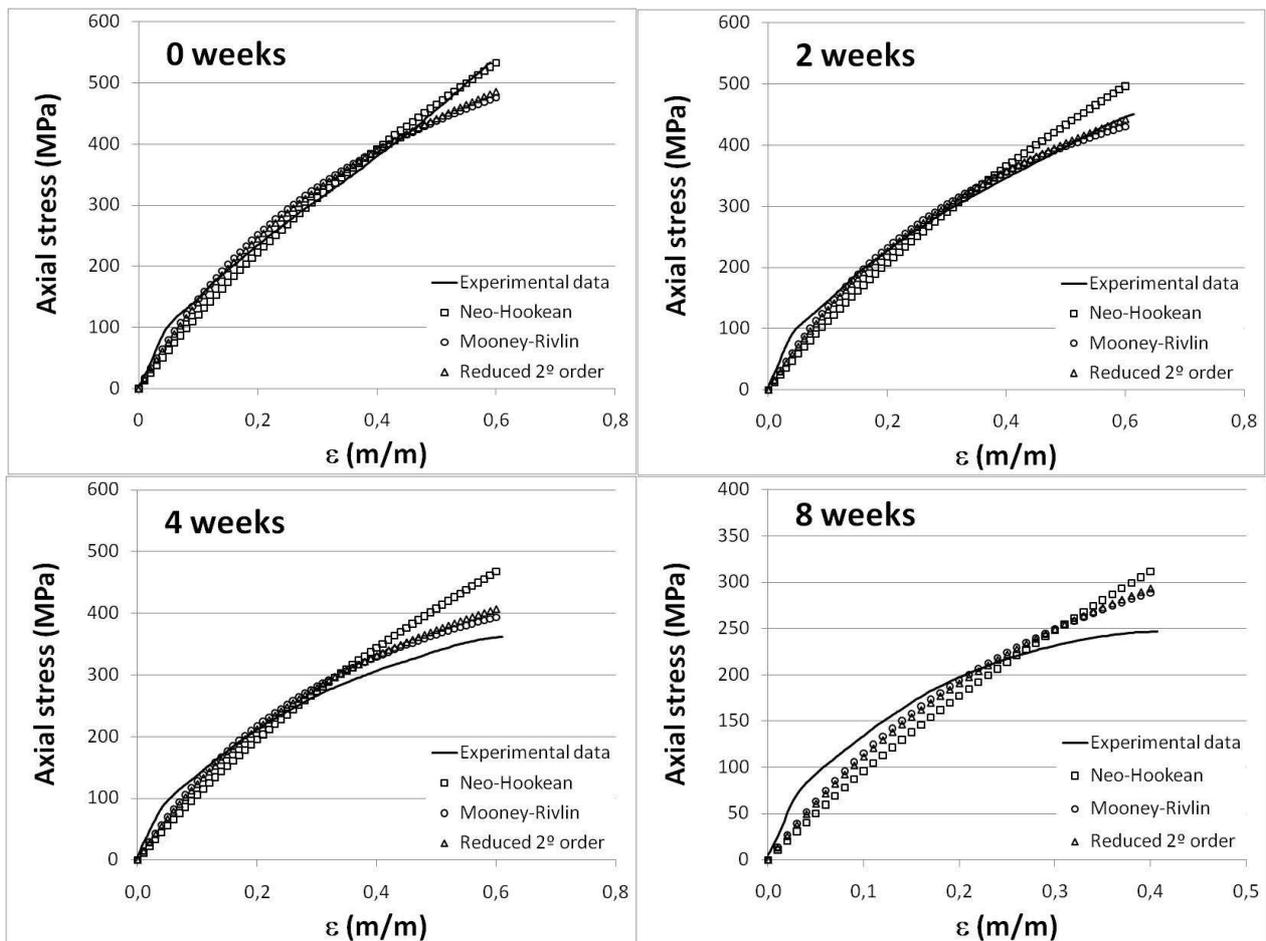


Figure 6. Axial nominal stress vs. strain for 0, 2, 4 and 8 weeks of degradation (experimental data and material models) (Vieira *et al.*, 2010)

These constitutive models may be implemented in commercial finite element software packages like ABAQUS, by changing the material parameter as function of hydrolytic damage or degradation time, and associated to the failure criterion implemented by a User Material (UMAT) subroutine.

#### 4. CONCLUSIONS

Although this method was only tested with this particular blend, the authors believe that this can be extended to other thermoplastic biodegradable materials with response similar to hyper elastic behavior. This method can also be applied to complicated numerical models in 3D applications, to predict its long-term mechanical behavior. The mechanical properties of aliphatic polyester and other biodegradable polymers are commonly assessed within the scope of linearized elasticity, despite the clear evidence that they are able, in the majority of the cases, to undergo large deformations. When loading conditions are simple and the desired life cycle is known, a “trial and error” approach may be sufficient to design reasonable reliable devices. In more complex situations, device designers can use numerical approaches to define the material formulation and geometry that will satisfy the initial requirements, without the occurrence of any degradation, using conventional dimensioning. However, the lack of design tools to predict long term behavior has limited the application of biodegradable materials. The development of better models for biodegradable polymers can enhance the biodegradable device design process. The considerations and the dimensioning methods presented here, may overcome this limitation. The simple material degradation model presented here, based on modifying the material parameters of the commonly used hyper elastic models as a function of degradation time, may enable a reasonably prediction of the life time of complex biodegradable devices.

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