Review

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Considerations for the design of polymeric biodegradable products

Abstract: Several biodegradable polymers are used in many products with short life cycles. The performance of a product is mostly conditioned by the materials selection and dimensioning. Strength, maximum strain and toughness will decrease along its degradation, and it should be enough for the predicted use. Biodegradable plastics can present short-term performances similar to conventional plastics. However, the mechanical behavior of biodegradable materials, along the degradation time, is still an unexplored subject. The maximum strength failure criteria, as a function of degradation time, have traditionally been modeled according to first order kinetics. In this work, hyperelastic constitutive models are discussed. An example of these is shown for a blend composed of poly(L-lactide) acid (PLLA) and polycaprolactone (PCL). A numerical approach using ABAQUS is presented, which can be extended to other 3D geometries. Thus, the material properties of the model proposed are automatically updated in correspondence to the degradation time, by means of a user material subroutine. The parameterization was achieved by fitting the theoretical curves with the experimental data of tensile tests made on a PLLA-PCL blend (90:10) for different degradation times. The results obtained by numerical simulations are compared to experimental data, showing a good correlation between both results.

Keywords: biodegradable; design; dimensioning; materials; selection.

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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. Important applications of these are found in the biomedical field, where biodegradable materials are applied on manufacturing scaffolds (biomedical devices) that temporarily replace the biomechanical functions of a biologic tissue, while it progressively regenerates its capacities. Moreover, biodegradable polymers can be applied for components of automobiles, trains and airplanes, in order to obtain “green products”, following ecological recommendations and eco-design philosophies. In the case of commodity products, biodegradable plastics claim clear environmental advantages in several short time applications, mainly in their final stage of life (waste disposal), which can clearly be evident through life cycle assessment.

However, the design process, using biodegradable polymers, is slightly more complex. It must contemplate the mechanical stress degradation, defined as the time-dependent cumulative irreversible damage, such as fatigue or creep damage and 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 products used during short periods. However, each of these may have some shortcomings, which restrict 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 [1] according to the application requirements, enabling a range of mechanical properties and degradation rates.

The most popular and important class of biodegradable synthetic polymers, is aliphatic polyesters, such as

polylactic acid (PLLA and PDLA), polyglycolic acid (PGA), polycaprolactone (PCL), polydioxone (PDO), polyhydroxyalkanoates (PHAs) and polyethylene oxide (PEO), among others. They can be processed as other thermoplastic materials and have been commonly used in biodegradable products. Hydrolytic and/or enzymatic chain cleavage of these materials leads to α -hydroxy acids, which, in most cases, are ultimately assimilated in the human body, or in a composting environment.

The poly- α -hydroxyesters, PLA, PGA and their copolymers, are the most popular aliphatic polyesters to have been synthesized for more than 30 years. The left-handed or levogyrous (L-lactide) and right-handed or dextrorotatory (D-lactide) are the two enantiomeric forms of PLA, with poly-D-lactide (PDLA) having a much higher degradation

rate than poly-L-lactide (PLLA). An intensive overview was done by Auras et al. [2]. 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, and is much more ductile than PLA [3]. PGA, since it is a hydrophilic material, may present a high degradation rate. The combination of PGA with PLA is usually employed to tune degradation rate [4]. PHAs make up 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

Table 1 Material properties of biodegradable thermoplastics: melting temperature (T_m), glass transition temperature (T_g), number average molecular weight (M_w), Young Modulus, tensile strength and maximum elongation.

Material	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	M_w (g/mol)	Young Modulus (MPa)	Tensile strength (MPa)	Maximum elongation (%)	Ref.
PLA	62	138	—	—	—	—	[6]
	—	—	—	3400	60	—	[7]
	59	—	3.34×10^5	—	—	—	[8]
	45–60	150–162	—	350–3500	21–60	2.5–6	[9]
	—	—	—	3300	57.8	—	[10]
PLLA	—	—	4.5×10^5	—	—	—	[11]
	53	170–180	—	—	—	—	[12]
	65	175	1.1×10^5	3200–3700	55–60	—	[13]
	55–65	170–200	—	2700–4140	15.5–150	3–10	[9]
	60	178	2×10^5	—	—	—	[14]
PGA	—	—	—	—	37	—	[15]
	35–45	220–233	—	6000–7000	60–100	1.5–20	[9]
PDO	—	—	1.5×10^5	—	139	62	[16]
PDLA	—	—	3.25×10^5	—	—	—	[17]
	51.6	—	—	2800	26	11.4	[18]
	50–60	—	—	1000–3450	27.6–50	2–10	[9]
PDLGA	—	—	1.2×10^5	—	—	—	[19]
PCL	–60	—	2.7×10^5	—	—	—	[17]
	—	53.1	2.7×10^4	—	—	—	[18]
	–60 to –65	58–65	—	210–440	20.7–42	300–1000	[9]
PDLA–PGA	–60	60	1.2×10^5	—	—	—	[14]
	40–60	—	—	1000–4340	41.4–55.2	2–10	[9]
PGA–PCL	—	—	1.5×10^5	—	192.1	55	[16]
PEO	—	—	3×10^5	—	—	—	[20]
	—	—	10^5 – 8×10^6	390	—	—	[21]
	–64	—	—	—	—	—	[22]
	5–15	168–182	—	3500–4000	40	5–8	[9]
PELA	—	—	—	14	26–31	—	[23]
PESu	–11.5	104	—	—	—	—	[24]
PPSu	–35	44	—	—	—	—	[24]
PBSu	–44	103	—	—	—	—	[24]

PBSu, poly(butylenes succinate); PCL, polycaprolactone; PDLA–PGA, blend of poly-L-lactide and polyglycolic acid; PDLGA, copolymer poly(DL-lactide-co-glycolic acid); PDLA, copolymer poly-DL-lactide; PDO, polydioxone; PELA, copolymer poly(ethylene oxide) and poly-L-lactide; PEO, polyethylene oxide; PESu, poly(ethylene succinate); PGA, polyglycolic acid; PHB, poly 3-hydroxybutyrate; PLA, polylactic acid; PLLA, poly-L-lactide; PPSu, poly(propylene succinate).

favorable mechanical properties and degradation times, within desirable time frames [5]. In Table 1, some physical properties are presented for different aliphatic polyesters. The information that can be found in literature, regarding physical properties, is still scarce and these depend on the molecular weight, the degree of purity, the blending compositions, the processing technologies, the crystalline degree, etc.

Natural polymers used in biodegradable products include starch, collagen, silk, alginate, agarose, chitosan, fibrin, cellulosic, hyaluronic acid-based materials, among others.

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. The mechanical behavior of biodegradable materials along its degradation time, which is an important aspect of the project, is still an unexplored subject. Many examples of this kind of design challenge can be found in the medical field (e.g., biomedical devices), ranging from biodegradable sutures [25], pins and screws for orthopedic surgery [26], local drug delivery devices [27], tissue engineering scaffolds [28], biodegradable ligaments [29], biodegradable endovascular [30] and urethral stents [31]. It is very important to mention that, nowadays, there is not an established scientific method to develop a product made from biodegradable polymers. Thus, scientific contributions in this direction can aid, not only the development of biomedical devices, but also components for automobiles, trains and airplanes.

Regarding the challenge presented above, in the first instance, this work will show the problems about degradation and erosion, demonstrating how these phenomena can be mathematically modeled. After that, hyperelastic constitutive models, such as the Neo-Hookean, the Mooney-Rivlin modified and the Second Reduced Order will be discussed, considering the biodegradation processes. Finally, an example of biodegradation process simulation is shown for a blend composed of PLLA and PCL. A numerical approach based on Finite Element Analyses, using ABAQUS, is presented, where the material properties of the proposed model are automatically updated corresponding to the degradation time, by means of a user material (UMAT) subroutine. The parameterization of the proposed material model for different degradation times was achieved by fitting the theoretical curves with the experimental data of tensile tests made on a PLLA-PCL blend (90:10). The results obtained by numerical simulations are compared to experimental data, showing a good correlation between both results.

2 Degradation and erosion

All biodegradable polymers contain hydrolysable or oxidizable bonds. Some others, mainly natural polymers, are also susceptible to enzymatic degradation, which depends on the enzymes present in the degradation media and the polymer affinity [32, 33]. This makes the material sensitive to moisture, heat, light, enzymes and also mechanical stress. These different types of polymer degradation (photo, thermal, mechanical and chemical degradation) can be presented alone, or combined, working synergistically to the degradation. Usually, the most important degradation mechanism of biodegradable polymers is chemical degradation via hydrolysis or enzyme-catalyzed hydrolysis [34] in the case of biomedical device applications. 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 susceptible to those enzymes. 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 [35, 36].

Another important distinction must be made between erosion and degradation. Both are irreversible processes. However, while the degree of erosion is estimated from the mass loss, or CO_2 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). Hence, the hydrolytic degradation process is included in the erosion process.

The erosion process can be described by phenomenological diffusion-reaction mechanisms, presented in Figure 1. Aqueous media diffuse into the polymeric material, while oligomeric products diffuse outwards to then be bio-assimilated by the host environment. Therefore, there is material erosion with corresponding mass loss. By contrast, 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, and so they degrade at the surface.

2.1 Diffusion

After immersion of a biodegradable polymeric product in an aqueous medium, the very first event which occurs

Figure 1 Scheme of erosion process [37].

is water uptake, up to a saturation level of water concentration. This maximum level of water concentration depends on the hydrophilicity of the polymer, its crystalline degree, temperature, pH and flow of the media. The penetrating water rapidly creates a negative gradient of water concentrations from the surface to the center, as expected from a pure diffusion viewpoint. However, this gradient vanishes in a couple of hours or days, when the specimen saturates. Diffusion of small molecules, e.g., 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 (T_g) and softening the material [38].

The water concentration (w) along the thickness (x), and during the incubation time (t), is determined using Fick's Eq. (1), presented for 1D:

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

or for 3D, using Eq. (2):

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

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, 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. If the behavior was initially brittle, there will be an increase in the brittleness. In Figure 2, a scheme is presented of the most common hydrolysis

Figure 2 Acid catalyzed hydrolysis mechanism [39].

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 split 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 [40]. According to Farrar and Gillson [41], the following, first-order Eq. (3), describes the hydrolytic process related to the carboxyl end groups (C), ester concentration (E) and water concentration (w), during the degradation time (t):

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

where u is the medium hydrolysis rate of the material, k is the hydrolysis rate constant, and 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 $C=1/M_n$, Eq. (3) becomes Eq. (4):

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

where M_n 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 $M_n=f(t)$. 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. [39], that the fracture strength follows the same trend as the molecular weight, described by Eq. (5):

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

The hydrolytic damage was defined by Vieira et al. [39], according to Eq. (6):

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

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, t . 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 versus bulk erosion

Different types of erosion are illustrated in Figure 3. One is homogeneous or bulk erosion without autocatalysis (Figure 3C), 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 3A), 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 Eq. (1) to calculate water concentration $w(t, x)$ at any instant time t through the thickness x , before using Eqs. (4) and (5). Surface eroding polymers have a greater ability to achieve zero-order release kinetics,

Figure 3 Schematic illustration of three types of erosion: (A) surface erosion, (B) bulk erosion with autocatalysis, and (C) bulk erosion without autocatalysis [39].

and are ideal candidates for developing products able to deliver substances such as drugs, aroma, fertilizers, etc [4]. Also, enzymatic erosion fits on this last type of erosion, since enzymes are unable to diffuse and present a raised hydrolysis kinetic constant k .

Surface and bulk erosion are ideal cases to which most polymers cannot be unequivocally assigned. The characteristic time of hydrolysis can be defined by Eq. (7), as the inverse of degradation rate:

$$\tau_H = \frac{1}{kEw} = \frac{1}{u} \quad (7)$$

If D is the diffusion coefficient of water in the polymer and L is the sample thickness, the characteristic time of diffusion can be defined by Eq. (8):

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

When $\tau_H \gg \tau_D$, water reaches the core of the material before it reacts, and the degradation starts homogeneously. When $\tau_H < \tau_D$, 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 is that the hydrolysis reaction is autocatalytic [42]. For example, a thick plate of PLA erodes faster than a thinner one made of the same polymer [43]. 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 [35]. As can be seen in Figure 3B, hollow structures are formed as a consequence [43].

3 Constitutive models for biodegradable materials

A constitutive model for a mechanical analysis is a relationship between the response of a body (e.g. 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 non-linear nature of the stress *versus* 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, the non-linear mechanical properties are usually represented in terms of a strain energy density function W , which is a scalar function of the deformation gradient. In this particular one dimensional case, W depends on the fiber stretch. 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 of the right Cauchy-Green deformation tensor in uniaxial tension are given by Eqs. (9) and (10):

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

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

where the axial stretch λ is related to the strain ε ($\lambda = 1 + \varepsilon$), and satisfies the condition $\lambda \geq 1$. For neo-Hookean incompressible hyperelastic solids, the stored energy function is given by Eq. (11):

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

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, in which the stored energy function is given by Eq. (12):

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

with two material properties μ_1 and μ_2 . Higher order stored energy functions may be considered to describe the experimental data, such as a reduced second order stored energy function, that includes a mixed term with both invariants of the right Cauchy-Green stretch tensor and an extra material constant μ_3 , in which the stored energy function is given by Eq. (13):

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

The axial nominal stress for the three models, neo-Hookean (σ^{NH}), Mooney-Rivlin (σ^{MR}) and Reduced Second Order ($\sigma^{2nd\ red}$), will be given by Eqs. (14), (15) and (16), respectively:

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

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

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

According to Soares et al. [44], 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. [39] determined that only the first material parameter, μ_1 , varies linearly with hydrolytic damage [as defined in Eq. (6)].

In fact, in this work, a blend of PLLA-PCL (90:10) was used in order to investigate the mathematical models discussed above. From Figure 4, one can see that the hyperelastic material models fit well the measured storage energy, for all of 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. It can be observed that the neo-Hookean model was the less precise. However, this model respects the Second Law of Thermodynamics, where every material parameters μ_i must be positive.

Therefore, it is recommended for developing products made from biodegradable polymers, using constitutive models, which changes the first material parameter with hydrolytic damage, i.e., $\mu_1(d_h)$, according to the linear regression (see Figure 5). This enables us to describe the mechanical behavior evolution by using Eqs. (14), (15) or (16), while the limit stress is defined by Eq. (5).

In a general case of 3D study, the first and second invariants of the deviatoric part of the left Cauchy-Green deformation tensor, are given by Eqs. (17) and (18):

$$I_B = \text{tr}(B) \quad (17)$$

$$II_B = 1/2[(\text{tr}B)^2 - \text{tr}B^2]^{1/2} \quad (18)$$

where B is the deviatoric stretch tensor ($B = FF^T$). The neo-Hookean compressible hyperelastic model is given by stored energy function, defined by Eq. (19):

Figure 4 Storage energy vs. axial stretch for 0, 2, 4 and 8 weeks of degradation [39].

Figure 5 Evolution of the material parameter, μ_1 , of the models during degradation [39].

$$W = (\mu_1/2)(I_B - 3) + K(J-1)^2 \quad (19)$$

where $\mu_1 > 0$ is the material property, usually called the shear modulus and K is a material constant that depends on the compressibility ($K=0$ for incompressible materials). J is the determinant of the deformation gradient ($J=1$ for incompressible materials) defined by Eq. (20):

$$J = \det(\partial x / \partial X) \quad (20)$$

where x is the current position of a material point and X is the reference position of the same point. Then, the deformation gradient with volume change eliminated is defined by Eq. (21):

$$F = J^{1/3}(\partial x / \partial X) \quad (21)$$

The Cauchy stress for the neo-Hookean model used in this work will be given by Eq. (22):

$$T = (\mu_1/J) \text{dev}(B) + 2C(J-1)I \quad (22)$$

where I is the second order identity tensor.

These constitutive models are not found in commercial finite element software. Therefore, it is recommended to implement them as a subroutine.

4 Numerical simulation of biodegradable polymers

As proposed by Vieira et al. [39], the simulation of biodegradable polymers requires that the first material parameter changes with hydrolytic damage, i.e., $\mu_1(d_h)$, according to a linear regression, which fits the material parameter μ_1 during degradation (Figure 5). Thus, the material model for predicting the life-cycle of a hydrolytic degradable product needs to be implemented by a subroutine. In the case of ABAQUS, it was possible to implement the neo-Hookean material model through a user material (UMAT) subroutine and PYTHON language. Therefore, the material parameter μ_1 was written as function of hydrolytic damage or degradation time. Also, a failure criterion was implemented in order to simulate a PLLA-PCL fiber behavior.

After the material model implementation, a 3D finite element model of a fiber was developed, using solid elements, which has parabolic interpolation functions with reduced and hybrid integration (designed by ABAQUS as C3D20RH). Thus a script was programmed in PYTHON language in order to obtain the numerical model. This script

Figure 6 Flow chart of operations done by ABAQUS/PYTHON and the UMAT subroutine [45].

is run by ABAQUS and the degradation time is required as an input parameter data (see Figure 6). The hydrolysis rate of the material (u) and the strength of the non-degraded material (σ_0) are initially set in the command lines. The material was considered nearly incompressible ($K=10^3$). Then, the script in PYTHON language calculates the hydrolytic damage (d_h) according to Eq (6), and the material strength (σ_t) according to Eq. (5), for a given degradation time (t). The script in PYTHON language also calculates the material parameter ($C_{10}=\mu_1/2$) as a function of the hydrolytic damage $C_{10}(d_h)$. The material strength (σ_t) and the material parameters (C_{10} and K) are considered input data for the UMAT subroutine, as shown in Figure 6.

Finally, the results obtained by the numerical simulations are compared to experimental data. Monotonic tensile tests were performed at 500 mm/min in suture fiber specimens, after 0, 2, 4 and 8 weeks of degradation under phosphate buffer solution at 37°C. Thus, from Figure 7, one can see that the implemented material model allowed a reasonable approximation of the tensile test results reported in the work of Vieira et al. [39]. It is important to verify that there is a convergence between the results close to the maximum force value, which is normally used as a criterion of design for biodegradable products, e.g., biomedical devices.

5 Conclusions

The mechanical properties of aliphatic polyester and other biodegradable polymers are commonly assessed within the scope of linearized elasticity, despite the clear evidence

Figure 7 Experimental vs. numerical results according of tensile tests to poly(L-lactide acid) (PLA)-polycaprolactone (PCL) fibers at different stages of hydrolytic degradation [45].

that they are able, in the majority of 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 products. In more complex situations, product designers should 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 product design process. The numerical approach presented here, based on the calculation of one material parameter of neo-Hookean hyperelastic model, which is a function of the degradation time, may overcome this limitation and enable a reasonable prediction of the life time of complex biodegradable products.

Moreover, although the implemented material model was only evaluated for this particular blend (PLLA-PCL), the authors believe that this can be extended to other thermoplastic biodegradable materials, with responses similar to hyperelastic behavior. This material model can be also applied to more complicated 3D geometries, in order to predict long-term mechanical behavior. Therefore, this work can aid not only the development of biomedical devices, but also components for automobiles, trains and airplanes.

This constitutive model was able to simulate the monotonic tensile test. Other more complex constitutive models, such as viscoelastic and viscoplastic models, can be used to simulate other loading cases, such as cyclic loading, creep or relaxation tests. In a recent study of Muliana and Rajagopal [46], a non linear viscoelastic model was used to model the time-dependent performance of biodegradable structures. In this work, they consider that hydrolytic damage depends both on the deviatoric strain tensor and the concentration of water. Hence, at each time increment step, hydrolytic damage must be calculated in the material point. First, water concentration at each material point is updated based on Fick’s law. Then, the hydrolytic damage is updated as a function of the deviatoric strain tensor. Finally, the constitutive relation is updated at each time increment step. This method enables modeling of the relaxation behavior (or creep) during degradation, and is reasonably good for modeling biodegradable structures undergoing moderate deformations.

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