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Deformation-induced hydrolysis of a degradable polymeric cylindrical annulus

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Abstract A thermodynamically consistent framework for describing the response of materials undergoing deformation-induced degradation is developed and applied to a particular biodegradable polymer system. In the current case, energy is dissipated through the mechanism of hydrolytic degradation and its effects are incorporated in the constitutive model by appropriately stipulating the forms for the rate of dissipation and for the degradation-dependent Helmholtz potential which changes with the extent of the degradation of the material. When degradation does not occur, the response of the material follows the response of a power-law generalized neo-Hookean material that fits the response of the non-degraded poly(L-lactic acid) under uniaxial extension. We study the inflation and extension of a degrading cylindrical annulus and the influence of the deformation on the mechanism of degradation and its consequent mechanical response. Depreciation of mechanical properties due to degradation confers time-dependent characteristics to the response of the biodegradable material: the material creeps when subjected to constant loads and stresses necessary to keep a fixed deformation relax.

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1 Introduction

The process of degradation of polymers, i.e. the loss of mechanical integrity due to extensive backbone chain scission, has received increased attention recently as there are several uses for such materials. Degradable polymers have found a wide variety of applications 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), and biodegradable endovascular and urethral stents (Colombo and Karvouni 2000; Tammela and Talja 2003). Polymers degrade by several different mechanisms, depending on their inherent chemical structure and the conditions to which they are subjected. Degradation results from an irreversible chemical change in the material which eventually leads to its breakdown or failure (Ottenbrite et al. 1992).

Degradation occurs because chemical bonds constituting the polymer chains have limited strength. For example, increases in temperature are associated with increase in energy of the vibrational state of the bonds, which can overcome the bond dissociation energy, and induce bond scission to occur. This process causes rapid decomposition of polymers at elevated temperatures (e.g. 500°C); but the pronounced temperature dependence of the rates of chemical reactions can cause significant degradation under much milder conditions. Some polymers undergo chemical reactions upon irradiation with ultraviolet or gamma rays, and certain naturally occurring polymers such as proteins or polysaccharides can be cleaved very effectively in the presence of specific enzymes (Schnabel 1981; Hawkins 1984; Gopferich 1997). Bond scission promoted by mechanical working also occurs (Booth 1963). Mechanical degradation has been utilized for processing natural rubber since the middle of the nineteenth century in a process called mastication. In the presence of air, it leads to a marked decrease in the average molecular weight of the rubber thus increasing its workability (Harmon and Jacobs 1966). Mechanical degradation of polymers in solution can be obtained with high-speed stirring, shaking, flowing through capillaries, turbulent flow, or ultrasonic treatment (Yu et al. 1979).

The prevailing mechanism of degradation of synthetic biodegradable aliphatic polyesters, the most common biodegradable polymer class for biomedical applications, is by random scission of the hydrolytically unstable backbone chain by passive hydrolysis when water is present (Weir et al. 2004). The rate of swelling of common aliphatic polyesters is usually higher than the rate of hydrolysis, hence the reaction occurs extensively through the swollen polymer bulk and the common mode of erosion observed in this class of polymers is bulk or homogeneous erosion (Gopferich 1997; Burkersroda et al. 2002).

Hydrolytic scission occurs spontaneously in the presence of readily available water and its rate is influenced by the microstructural properties of the molecular network: (i) dramatic changes in the network morphology occur as a consequence of conformational changes in the polymer chains in response to bulk deformations [e.g. uniaxial tensile strains have been found to be responsible for causing strain induced crystallization (Kannan and Rajagopal 2005)]; (ii) the crystalline phase is generally more resistant to degradation than the amorphous phase, a phenomenon attributed possibly due to differences in bond availability, steric hindrance, or changes in local hydrophilicity (Gopferich 1997); (iii) the amount of swelling of polymeric networks can be inhomogeneously distributed over the polymer bulk in response to the deformations to which the polymer bulk is subjected. See Baek and Srinivasa (2004) and Soares (2009) for a single-constituent model that describes such phenomenon, or (Rajagopal 2003) and references therein for the mixture theory approach to tackle the problem of swelling. Finally and most important, (iv) experimental evidence shows that deformation and degradation are coupled processes.

Miller and Williams (1984) carried out one of the early studies on the effect of imposed strain on the degradability of a commercially available poly(glycolic acid) used for surgical sutures. A special device (suited either for in vitro, in aqueous media, and in vivo, implanted subcutaneously in rabbits) was designed such that the sutures could be maintained under a state of uniaxially applied strain of 25 and 50% of the breaking strain of the non-degraded material. Stress relaxation was observed during degradation—after 14–21 days, no tension was necessary both in vivo and in vitro experiments. Degradation was assessed by measurements of the load at breaking and the ability of the degradable material to withstand load was significantly decreased by the magnitude of the imposed strain during the course of degradation. Similarly, Chu (1985) reported that immersed and strained poly(glycolic acid) fibers degraded faster (i.e. lost mechanical integrity faster) than unstrained ones, and the magnitude of degradation depended on the level of the strain applied and the duration of immersion. Zhong et al. (1993) imposed a 4% strain, with a slightly different suture material (90–10% poly(glycolic-lactic acid)): after two weeks of accelerated degradation in hydrogen peroxide (which allows hydrolysis and oxidation degradation pathways to coexist), they concluded that the degradation of the suture under strain was much faster than without strain. Furthermore, the applied strain itself, in the absence of a chemically reactive environment, did not change the mechanical properties of the suture. With polyurethane (on which the degradation mechanism is oxidation), Wiggins et al. (2003) found that the degradation rate of polyurethane increased with increasing cyclic strain rate, while the magnitude of the strain had essentially no effect. Their experiments employed a circular membrane device in which pressure was applied to one side of the membrane, causing it to deflect into a well. Under this deformation, a state of bi-axial strain exists in the middle region of the membrane, and mostly a uniaxial strain state in the outer region. They demonstrated that the polymer in the cyclic uniaxial strain region degraded at the same rate as those that were unstressed or under constant stress. However, polymer in the biaxial strain region degraded at a much higher rate (Wiggins et al. 2004).

The influence of the mechanical environment on the rates of degradation of stable polymers has long been studied by the polymer physics and chemistry community, especially for dilute polymers under solution with application as drag reducers in turbulent flows or as viscosity index improvers for motor oils (Booth 1963; Yu et al. 1979). On the other hand, the influence of mechanical loading on degradable polymers, which unquestionably exhibit chain scission by chemical degradation and are designed to perform under mild to severe loading conditions (such as aliphatic polyesters employed in the biomedical field), have not been the object of much research.

The development of better models for biodegradable materials can enhance the implantable device design process. When loading conditions are simple and the desired time of mechanical support is fairly well known, a “trial and error” approach for the design has proven to be sufficient in producing reasonably reliable biodegradable biomedical devices. In more complex situations, device designers must try to guess the material formulation and geometry that will satisfy the immediate needs of symptomatic relief, yet continue to provide function for an appropriate period. The lack of rational design tools has severely limited the application of biodegradable materials in these situations.

In order to understand the applicability and efficacy of this class of materials, a two-pronged approach involving experiments and theory is necessary. Recent theoretical developments with the goal towards explaining such a class of materials has been initiated by Rajagopal et al. within a consistent thermodynamic framework wherein it is only necessary to stipulate how the material stores and dissipates mechanical energy (Rajagopal et al. 2007; Rao and Rajagopal 2007). The basis for such models for the degradation of polymeric solids can be traced back to the work of Rajagopal and Wineman on two network models, which allow for scission and healing (the formation of new networks in new natural states) dependent on a state variable that locally measures the extent of deformation (Rajagopal and Wineman 1992; Wineman 2001). Based on phenomenological reasoning, Soares (2008) and Soares et al. (2008) have developed similar models suitable for deformation-induced degradable materials.

The vast majority of experimental efforts on aliphatic polyesters have been directed towards varying formulations and product development. Mechanical properties are commonly assessed within the scope of linearized elasticity, despite clear evidence that they are capable of undergoing large deformations. More importantly, the investigation of the evolution of degradation is usually limited to unloaded specimens and analyzed through the evolution of scalar averages of the molecular weight distribution, mass loss, and simple mechanical quantities, such as Young's modulus and tensile strength.

The goal of this study is to shed additional light on the relationship between deformation and degradation in the case of a polymeric cylinder subjected to a pressure load and an axial stretch. In this paper, we obtain a class of models for degradable polymers consistent with the thermodynamic framework for deformation-induced degradation by Rajagopal et al. (2007) and the phenomenologically based models by Soares (2008) and Soares et al. (2008). When degradation does not occur, the body responds elastically. In this study, the constitutive relationship describing the response of the non-degraded material was obtained from uniaxial extension experiments with poly(L-lactic acid) fibers. In this case, the power law material proposed by Knowles (1977) is appropriate to describe the elastic response of poly(L-lactic acid).

The initial and boundary value problem under consideration is the inflation and extension of a cylindrical annulus, which is a choice motivated by its appearance in a variety of biomedical applications. As application of such geometries within the context of biodegradable polymers in the medical field, one can list biodegradable scaffolds for tissue engineering of arteries and biodegradable stents (either cardiovascular or urethral, although in these cases deflation occurs). This inhomogeneous motion not only confers sufficient complexity to the problem, but also allows the equations it yields to be solved numerically with ease. Lastly, results obtained with this initial and boundary value problem are useful for the validation of the implementation of this biodegradable constitutive model into finite element software packages.

In this analysis, we shall ignore other scission pathways besides hydrolysis and concentrate our attention on changes in the hydrolysis rate due to the imposed mechanical environment, i.e. strain-modulated degradation. We view this as a first step towards a more detailed constitutive model for biodegradable poly(L-lactic acid) that would include changes in temperature, amount of swelling and diffusion of water and degradation byproducts within the degrading polymer matrix. These entropy producing phenomena would have to be characterized by different specifications of how the material dissipates energy.

2 Preliminaries

Let $\mathbf{X}$ denote a typical point belonging to the reference configuration κ_R and $\mathbf{x}$ the same material point at time t, belonging to current configuration κ_t. Let $\mathcal{X}_{\kappa_R}$ denote a one-to-one mapping that assigns to each $\mathbf{X} \in \kappa_R$ a $\mathbf{x} \in \kappa_t$, i.e.

$$\mathbf{x} = \mathcal{X}_{\kappa_R}(\mathbf{X}, t). \tag{1}$$

We shall assume that $\mathcal{X}_{\kappa_R}$ is a sufficiently smooth mapping. The deformation gradient $\mathbf{F}$ and the left Cauchy-Green stretch tensor, $\mathbf{B}$, are respectively

$$\mathbf{F} \equiv \frac{\partial \mathbf{x}}{\partial \mathbf{X}}, \quad \mathbf{B} = \mathbf{F}\mathbf{F}^{\mathrm{T}}. \tag{2}$$

The Cauchy stress field in the body is denoted by $\mathbf{T}$ and we assume that the local form of the balance of mass, linear momentum (in the absence of body forces) and angular momentum are given respectively by

$$\dot{\rho} + \rho \operatorname{div} \mathbf{v} = 0, \tag{3}$$

$$\operatorname{div} \mathbf{T} = \rho \ddot{\mathbf{x}}, \tag{4}$$

$$\mathbf{T} = \mathbf{T}^{\mathrm{T}}, \tag{5}$$

where ρ stands for the current mass density (mass per unit current volume), the superposed dot indicates the material time derivative, and the notation div stands for the divergence operator with respect to current coordinates.

3 Constitutive model

We begin the modeling by introducing a scalar variable d which represents the degree of degradation at a particle,

$$d = d(\mathbf{x}, t). \tag{6}$$

Degradation d is the amount of degradation of particle that is at point $\mathbf{x}$ at time t and takes the value between zero and unity. Consequently, $1-d$ is a measure of the fraction of intact cross-links of that particle. The value $d=0$ represents a virgin state whereas $d=1$ represents a state with no degradable cross-links left. Degradation occurs due to chain scission through hydrolysis, a chemical reaction, thus d plays the role of a reaction variable.

For the isothermal processes under consideration, the Helmholtz potential ψ of the degradable network is a function of the deformation gradient $\mathbf{F}$ and the degree of degradation d so that

$$\psi=\psi(\mathbf{F},d). \tag{7}$$

It is common practice in developing constitutive theories to stipulate the constitutive equations for the stress in terms of the derivatives of ψ as well as for the reaction rate, with coefficients such that the second law of thermodynamics is not violated. Phenomenologically derived models of this kind were studied by Soares (2008) and Soares et al. (2008).

Rajagopal et al. (2007), within a general framework for the study of dissipative processes developed by Rajagopal et al. (cf. e.g. Rajagopal and Srinivasa 2004; Rao and Rajagopal 2007), considered the reduced energy dissipation equation as a restriction on allowable processes. The functional form of the rate of dissipation, ξ, was chosen to be

$$\xi=\xi(\mathbf{F},d,\dot{d}), \tag{8}$$

and constitutively stipulating the forms of ψ and ξ, i.e. how energy is stored and dissipated, suffices to describe the response of materials that suffer deformation-induced chain scission and its effect on the mechanical response. Maximizing the rate of dissipation over all allowable processes subject to (7) and incompressibility as constraints leads to the specific form of the stress

$$\mathbf{T}=-p\mathbf{1}+\rho\frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^{\mathrm{T}}, \tag{9}$$

where p is a Lagrange multiplier enforcing the constraint of incompressibility, and to a governing equation for the evolution of degradation

$$-\rho\frac{\partial\psi}{\partial d}\dot{d}=\xi. \tag{10}$$

4 Special constitutive assumptions

The entire structure of the constitutive equations can be obtained once specific forms for ψ and ξ are chosen. Rajagopal et al. (2007) obtained a model for a material whose elastic response is neo-Hookean-like when there is no degradation, and whose shear modulus decreases linearly with the degree of degradation. Rajagopal et al. (2007) assumed a rate of dissipation of the form

$$\xi=D_0\left\|\dot{d}\right\|+D_1\frac{\left\|\dot{d}\right\|^{\frac{n+1}{n}}}{(1-d)^{1/n}}, \tag{11}$$

where D_0 and D_1 are constants, and n characterizes the power law behavior of the rate of dissipation. Such rate of dissipation functions are characteristic of threshold or yielding behavior. Note that as d tends to one, the rate of dissipation ξ increases to infinity. Nevertheless, for the state of maximum degradation to be reached, the driving force must become infinite, which is not achievable. Equation (10) with (11) yields

$$\dot{d}=\left\{\frac{D-D_0}{D_1}\right\}^n(1-d),\ \text{if } D>D_0, \tag{12}$$

where

$$D\equiv-\rho\frac{\partial\psi}{\partial d} \tag{13}$$

is defined as the driving force for degradation.

Constants D_0, D_1 and n describe the entropy producing process. D_0 is a threshold driving force necessary for degradation to occur and responsible for branching of the response (Rajagopal and Wineman 1980): if $D>D_0$, the material degrades following (12); on the other hand, if $D\leq D_0$, the driving force is not sufficient for scission to happen, there is no further degradation and the material responds perfectly elastically accordingly to the current level of degradation (Rajagopal et al. 2007). D_1 is associated with the intrinsic time scale of degradation $(D_1/\mu_0)^n$, where μ_0 is a representative modulus of the material.

One particularization of this model was used by Soares et al. (2008). Note that with $n=1$, (10) with (11) can be cast into the form

$$\dot{d}=(1-d)\mathcal{K}(\mathbf{F}), \tag{14}$$

where $\mathcal{K}(\mathbf{F})$ can be seen as a deformation-dependent reaction rate. Selectivity can be conferred on $\mathcal{K}(\mathbf{F})$ either by picking a threshold value or with the aid of an activation criterion.

In this particular paper, we will employ the class of materials introduced by Knowles (1977), whose stored energy function is of the form

$$\rho\psi(\mathbf{F})=\frac{\mu}{2b}\left[\left(1+\frac{b}{m}(I_{\mathbf{B}}-3)\right)^m-1\right]. \tag{15}$$

Constant μ is the shear modulus, and b and m are dimensionless positive material constants. A material following (15) is of the hardening type in simple shear if $m>1$. If $m=b=1$, the classical neo-Hookean model is recovered.

We found constitutive relation (15) to be useful to describe the mechanical response of poly(L-lactic acid) under isochoric uniaxial extension. Poly(L-lactic acid) is widely regarded as an incompressible material (Lunt 1988; Garlotta 2001), and the uniaxial stress T vs. uniaxial stretch λ is given by

$$T = \mu\left[1 + \frac{b}{m}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)\right]^{m-1}\left(\lambda^2 - \frac{1}{\lambda}\right). \tag{16}$$

The degradation of a given particle and its consequent molecular weight reduction leads to depreciation in the mechanical properties of the corresponding particle. The Cauchy stress in a degradable material is given by Eq. (9) and the Helmholtz potential that characterizes the constitutive models of interest is made to depend on the degradation parameter, i.e. $\psi = \psi(\mathbf{F}, d)$. Constitutive Eq. (15) involves a set of material parameters $\{\mu, b, m\}$ and the effect of degradation is depicted as changes in the material properties that characterize the response of the biodegradable material. More precisely, the material parameters are considered to be material functions of degradation instead of material constants, i.e. $\{\mu = \mu(d), b = b(d), m = m(d)\}$.

The particular form of the material functions is arbitrary; the only restriction is that they are strictly positive, a requirement of the constitutive law. Due to the unavailability of experimental data, a simple linear variation from values that characterize the non-degraded response $\{\mu_0, b_0, m_0\}$ towards values that describe the response of the material in the maximum achievable degradation state $\{\mu_1, b_1, m_1\}$ (as $d \to 1$) is considered, i.e.

$$\mu(d) = \mu_0\left[1 - \left(1 - \frac{\mu_1}{\mu_0}\right)d\right], \tag{17}$$

$$b(d) = b_0\left[1 - \left(1 - \frac{b_1}{b_0}\right)d\right], \tag{18}$$

$$m(d) = m_0\left[1 - \left(1 - \frac{m_1}{m_0}\right)d\right]. \tag{19}$$

Stress vs. strain data obtained experimentally with non-degraded PLLA (cf. (Soares 2008)) can be reduced with (16) such that the constants $\{\mu_0, b_0, m_0\}$ that characterize the response of non-degraded PLLA are obtained (Table 1; Fig. 1). A parametric study on the influence of each material parameter reveals that m is generally related with the type of the response (hardening if $m > 1/2$ and softening if $1/2 > m > 0$) while b and μ are related with the absolute value of stress achieved in the material (cf. Fig. 2 and Fig. 3 from Knowles (1977) for the responses of the material subjected to simple shear and isochoric uniaxial extension, the latter in Eq. 16).

Table 1 Material constants that characterize the instantaneous elastic response of non-degraded PLLA, based on the experimental data shown in Fig. 1

μ_0	233.20 MPa
b_0	777.33
m_0	0.5278

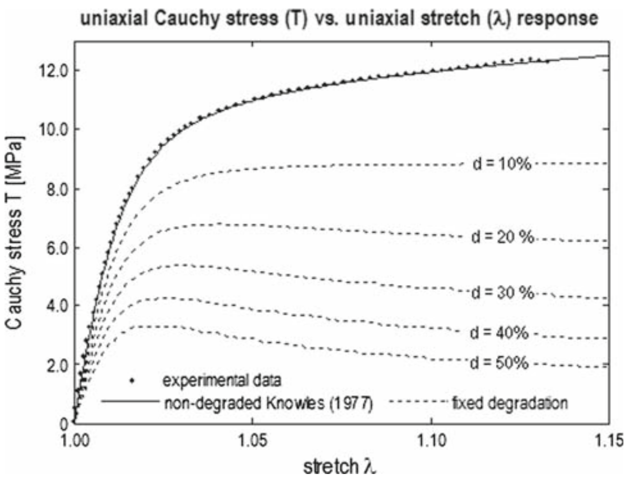

Fig. 1 Instantaneous elastic response of non-degraded semi-crystalline PLLA samples (cf. Soares 2008). The power law material (Eqs. 15 and 16) leads to a very good description of the response of the non-degraded material when subjected to uniaxial extension. The family of responses of the degrading polymer at different levels of degradation is also shown as *dashed lines*. Note that increasing degradation leads to a change in the overall stiffness of the material

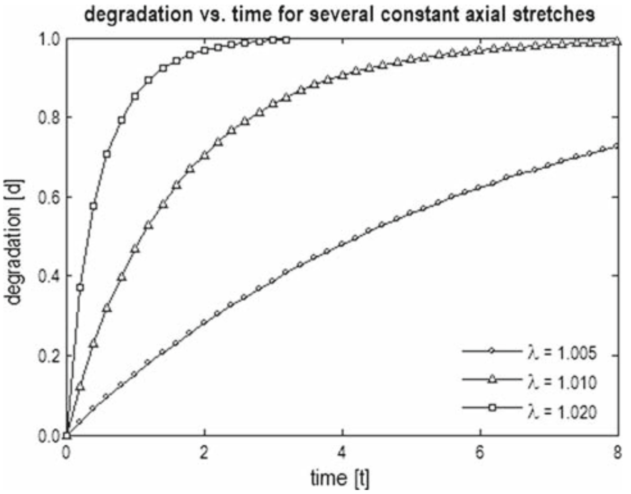

Fig. 2 Degradation for several constant axial stretches in the degradable cylindrical annulus undergoing pure extension. The axial stretch is responsible for a homogeneous deformation which promotes the increase of degradation uniformly. Due to constitutive specifications, the degradation tends asymptotically to its maximum value when the material is subjected to a constant deformation. For greater stretches, the material degrades at a faster rate

Thus, in the absence of experimental data and to further particularize the degradable material described by (15) and material functions (17)–(19), we choose $\mu_1 = b_1 = m_1 = 0$, such that as $d \to 1$ the Helmholtz potential $\psi(\mathbf{F}, d) \to 0$, i.e. as degradation proceeds, the material loses its ability to store energy. The family of responses of such material behavior corresponding to different levels of degradation is shown in Fig. 1.

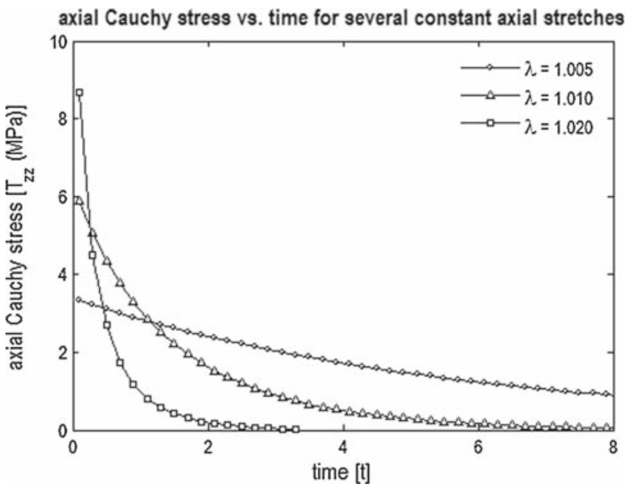

Fig. 3 Axial Cauchy stress required to maintain a constant axial stretch. Stress relaxation occurs due to degradation. When the material is fully degraded, it loses its ability to withstand load and the required force decays to zero. Higher initial stretches lead to a greater rate of degradation and thus a shorter time to effective material breakdown

The driving force for degradation, defined in (13), is given by

$$D = \frac{\mu_0 m_0}{2b_0}\left[1 + \frac{b_0}{m_0}(I_{\mathbf{B}} - 3)\right]^{m_0(1-d)} \ln\left(1 + \frac{b_0}{m_0}(I_{\mathbf{B}} - 3)\right). \tag{20}$$

Note that when the body is undeformed, $I_{\mathbf{B}} = 3$ and consequently $D = 0$. Furthermore, the form of the driving force of degradation is dramatically simplified if $\mu_1 = b_1 = m_1 = 0$, yielding the single term present in Eq. (20).

5 Inflation and extension of a degradable cylindrical annulus

We shall consider the annular region between two co-axial right circular cylinders of inner and outer radii R_i and R_o. The motion (in cylindrical polar coordinates) of the form

$$r = r(R, t), \theta = \Theta, z = \lambda(t)Z, \tag{21}$$

is sought. (R, Θ, Z) represents the coordinates of a particle in the reference configuration in cylindrical polar coordinates and (r, θ, z) represents the coordinates of the particle at time t. Function of time $\lambda(t)$ denotes the uniform extension along the direction of the axis of the cylindrical annulus whereas the function $r(R, t)$ describes the inflation or deflation of the annular region.

The deformation gradient $\mathbf{F}$ and the left Cauchy-Green stretch tensor $\mathbf{B}$ are obtained through Eq. (2) and in a cylindrical coordinate system have matrix representations given by

$$(\mathbf{F}) = \begin{pmatrix} r_{,R} & 0 & 0 \\ 0 & \frac{r}{R} & 0 \\ 0 & 0 & \lambda \end{pmatrix}, \quad (\mathbf{B}) = \begin{pmatrix} r_{,R}^2 & 0 & 0 \\ 0 & (\frac{r}{R})^2 & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}, \tag{22}$$

respectively. Notation $(\cdot)_{,R}$ denotes $\partial(\cdot)/\partial R$. For this deformation,

$$I_{\mathbf{B}} \equiv \operatorname{tr} \mathbf{B} = r_{,R}^2 + \left(\frac{r}{R}\right)^2 + \lambda^2, \tag{23}$$

and

$$III_{\mathbf{B}} \equiv \det \mathbf{B} = \left(\lambda \frac{r}{R} r_{,R}\right)^2. \tag{24}$$

Because $III_{\mathbf{B}} > 0$ and if inversion of the cylinder is not allowed, it immediately follows that $r_{,R} > 0$. The bodies of interest are assumed to be incompressible, hence (22) yields a condition that the motion must satisfy for all t, i.e.

$$J \equiv \det \mathbf{F} = 1. \tag{25}$$

Constraint (25) can be integrated directly to yield the radial relationship between the reference and the current configurations, i.e.

$$r(R, t)^2 = r(R_i, t)^2 + \frac{R^2 - R_i^2}{\lambda(t)}, \tag{26}$$

where current location of inner radius $r_i(t) = r(R_i, t)$ is the unknown function of time appearing due to integration.

The stress field is obtained through the constitutive equation (9) and the Helmholtz potential (15). Usual time scales of degradation of poly(L-lactic acid) are on the order of months to weeks (Lunt 1988; Garlotta 2001); hence, we will assume that mechanical loading and deformation occur in an infinitely slow process such that motions are quasi-static. The linear momentum balance (4) upon change of differentiation from the current configuration to the reference configuration yields

$$\frac{T_{rr,R}}{r_{,R}} + \frac{1}{r}(T_{rr}^e - T_{\theta\theta}^e) = 0, \tag{27}$$

where the decomposition $\mathbf{T} = -p\mathbf{1} + \mathbf{T}^e$ is used. One finds convenient to consider Eq. (27) upon integration from to inner radius R_i to R, i.e.

$$T_{rr}(R, t) = T_{rr}(R_i, t) + \int_{R_i}^{R} \frac{r_{,R}(s, t)}{r(s, t)}[T_{\theta\theta}^e(s, t) - T_{rr}^e(s, t)]\mathrm{d}s. \tag{28}$$

The boundary conditions are of the type

$$\mathbf{t}|_{R=R_i} = P_i(t)\mathbf{e_r} \Rightarrow -T_{rr}(R_i, t) = P_i(t), \tag{29}$$

$$\mathbf{t}|_{R=R_o} = -P_o(t)\mathbf{e_r} \Rightarrow T_{rr}(R_o, t) = -P_o(t), \tag{30}$$

i.e. known normal pressures are applied to the inner and outer part of the cylinder. Hence, considering the case when

$R = R_o$, Eq. (28) becomes

$$\Delta P(t) = P_i(t) - P_o(t) = \int_{R_i}^{R_o} \frac{r_{,R}(s,t)}{r(s,t)} [T^e_{\theta\theta}(s,t) - T^e_{rr}(s,t)] \mathrm{d}s, \quad (31)$$

which holds for all time t. Equation (31) is solved numerically for each time t for $r_i(t) = r(R_i, t)$. Once the position of the inner surface is known, the Lagrange multiplier can be obtained with Eq. (26) through

$$p(R,t) = P_i(t) + T^e_{rr}(R,t) - \int_{R_i}^{R} \frac{r_{,R}(s,t)}{r(s,t)} [T^e_{\theta\theta}(s,t) - T^e_{rr}(s,t)] \mathrm{d}s, \quad (32)$$

and then, the entire stress field follows from constitutive Eq. (9) with Helmholtz potential (15).

For the case of degradable bodies, the equation governing degradation (10) is coupled to the balance of linear momentum and degradation d is the extra unknown that needs to be determined. Extra stresses in Eq. (31) become dependent on current degradation and the problem becomes nonlinear. An initial condition regarding the extent of degradation is necessary and we simply assume that the cylindrical annulus starts out uniformly non-degraded, i.e. $d(\mathbf{X}, 0) = 0$. Equation (12) with D given by (20) is solved using a fourth order Runge-Kutta method starting from the initial condition.

The inner radius of the annulus was chosen to be $R_i = 2.4$ mm and its thickness is 100 μm. These dimensions are indicative of a small caliber tissue engineered vascular graft for coronary bypass surgery. Constants appearing in the rate of dissipation (Eq. 11) are assumed to be $D_0 = 0$, $D_1 = 1 \cdot 10^5$, and $n = 1$. A parametric study on the influence of such constants is complex and relevant but it was chosen not to be included within this study (cf. Rajagopal et al. (2007) for the effects of different n on the response of a degrading beam). We were mainly concerned with the mechanical response of a degradable cylindrical annulus in response to different loading conditions rather than the analysis of variations in specific material properties.

Standard values for the transmural pressure and the axial extension are $\Delta P = 100$ kPa and $\lambda = 1.01$, respectively; and deviations from these values will be parametrically investigated. These values were chosen in order to promote a deformation, that in conjunction with rate D_1, provides that breakdown of the material and consequent failure of the numerical scheme (as $\psi \to 0$) occurs within a reasonable upper bound of the natural time scale of degradation defined by D_1 and $\psi(\mathbf{F}, d = 0)$.This is important for a feasible discretization of time in the numerical scheme, which is normalized with respect to characteristic degradation time.

6 Results

The results shown in this section are split into three main cases: (i) the annulus is subjected to several constant axial stretches (a homogeneous deformation) and its mechanical response and degradation is analyzed; (ii) a similar procedure is followed for the pure inflation of the degradable annulus subjected to constant transmural pressures; and, (iii) the annulus is subjected to axial extension and pure inflation concomitantly.

6.1 Axial extension of a degradable cylindrical annulus

Under a state of axial extension characterized by a constant axial stretch, degradation shows an asymptotic increase towards its maximum allowable value (Fig. 2). The state of degradation is exactly the same in all particles of which the annulus is composed. Moreover, the stress necessary to maintain the constant axial stretch decreases, i.e. stress relaxation is observed (Fig. 3). The time course of degradation is directly related to deformation that is imparted in the annulus, i.e. more stretch leads to a faster degradation.

6.2 Pure inflation of a degradable cylindrical annulus

Under the influence of constant inflation, the annulus consistently increases its radius over time (Fig. 4). The extent of this creep-like behavior is dependent on the amount of degradation, which increases progressively till failure (depicted in Fig. 5): when subjected to the same inflation pressure, a more

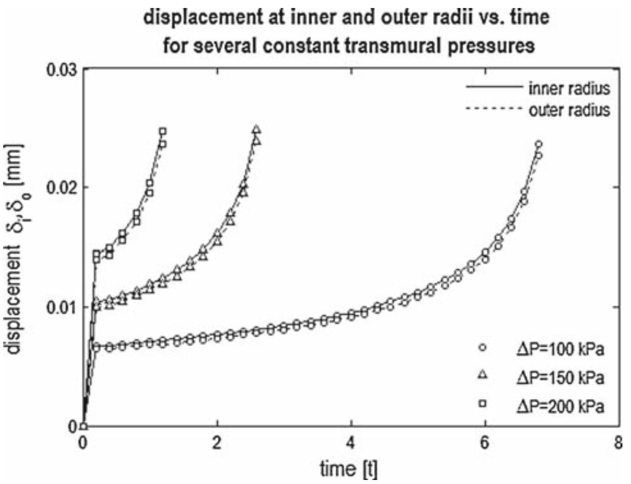

Fig. 4 Displacement of the inner and outer surfaces for several transmural pressures in a degradable cylindrical annulus undergoing pure inflation. Upon initial inflation, the annulus deforms to a certain extent determined by the initial (non-degraded) material properties. With degradation, the deformation achieved by the same inflation pressure increases steadily, i.e. the annulus creeps

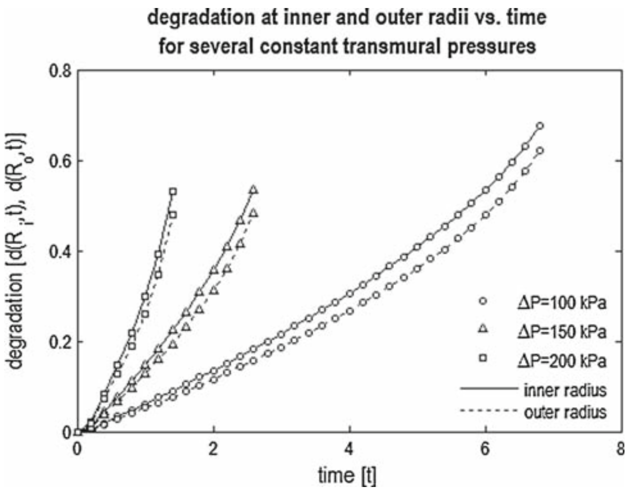

Fig. 5 Degradation at the inner and outer radii for several constant transmural pressures in a degradable cylindrical annulus undergoing pure inflation. Degradation is more aggressive near the inner wall. Degradation increases steadily due to a constant transmural pressure. As the material loses its ability to withstand load, the annulus undergoes greater inflations that are responsible for greater degradation rates

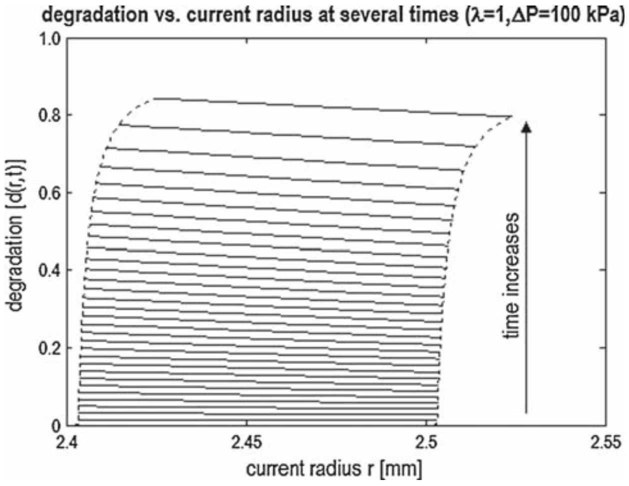

Fig. 6 Degradation versus current radius at several instants of time for a degradable cylindrical annulus undergoing pure inflation. Degradation is more aggressive near the inner wall where the material is more circumferentially stretched. Initially, degradation is nearly homogeneous, but as time proceeds, degradation gradients across the annulus become more intense

degraded material will deform to a greater extent, which in turn will lead to a stronger increase in degradation.

When subjected to this type of deformation, the cylindrical annulus does not degrade homogeneously. Portions near the inner wall degrade faster and to a higher extent because the state of local deformation in this region is harsher when compared to the region near the outer wall (Fig. 6). This results in material properties being non-homogeneous across the thickness after the onset of degradation, even though the material started out as a homogeneous body.

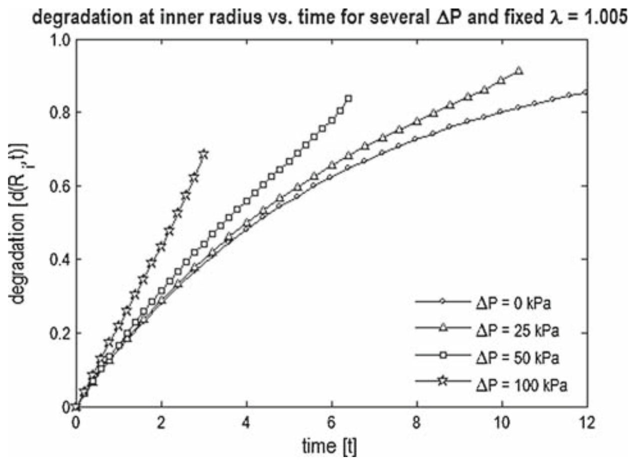

Fig. 7 Degradation at the inner radius for a degradable cylindrical annulus subjected to axial extension and several inflation pressures. Under uniaxial extension, degradation increases towards its maximum (cf. Fig. 2). When a constant inflation pressure is also applied to the material, the mode of increase of degradation changes abruptly, i.e. it no longer asymptotically approaches the maximum value. In fact, as inflation pressure increases, the shape of the curve resembles exponential increase towards failure (cf. Fig. 4), as inflation becomes responsible for the majority of the deformation that drives the increase of degradation

6.3 Inflation and extension of a degradable cylindrical annulus

When inflation is accompanied with extension, the increase in degradation is a combination of concurrent characteristics of the two previously mentioned cases.

With a constant axial stretch, degradation increases asymptotically to its maximum value (Figs. 2, 7), but as soon as an inflation pressure is applied to the annulus, a shift in the pattern of the increase of degradation is observed: as the material properties decrease, the same inflation pressure is able to deform the material to a great extent and its effect on the rate of deformation induced-degradation becomes more acute than the constant axial extension (Fig. 7).

A similar effect is obtained with the converse situation (Fig. 8): starting from the progressive increase of degradation and deformation when constant transmural pressure is applied, significant increases in axial stretch promote an initial shift in the pattern of the increase of degradation. Nevertheless, as the mechanical properties decrease, the constant inflation will become the dominant factor of the overall deformation and the annulus will consequently fail.

7 Discussion

The ability to model the behavior of biodegradable polymers subjected to mechanical loads would enhance the predictive nature of biodegradable implants design. Several constitutive

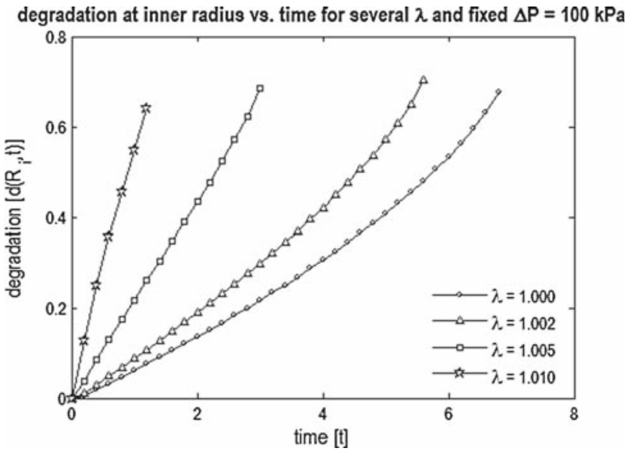

Fig. 8 Degradation at the inner radius for a degradable cylindrical annulus undergoing inflation and extension (for fixed transmural pressure and several axial stretches). The curves associated with the more intense axial stretches share an initial resemblance with the ones presented in Fig. 2. Nevertheless, due to the inflation pressure, the annulus will eventually creep, and as the material degrades, this effect becomes more intense and eventually dominates the final shape of the curves

assumptions were considered in the previous sections and the resulting thermodynamically consistent constitutive model for deformation-induced degradation provides, qualitatively, phenomenological support. Degradation is quantified by a parameter that describes locally the amount of degradation and changes the mechanical properties through a Helmholtz potential that is dependent on the degradation parameter (cf. Eq. (7)). The body starts out in a virgin state and due to the deformation it is subjected to (either through imposed stretches or imposed loads), it degrades. The results indicate an increase in degradation (Figs. 2, 5, 6, 7, 8) and consequent decrease in material moduli (cf. Fig. 1).

The current model is based on two key assumptions: (i) the second law of thermodynamics as a restriction on allowable processes; and (ii) the assumption that the allowable processes maximize the rate of dissipation ξ, which functions as a selectivity criterion for the response of the material to "branch" or switch between its elastic response and a dissipative response which involves the increase of degradation (cf. Eq. 12). The constitutive theory is then solely determined by the specification of the form of the Helmholtz potential ψ and the rate of dissipation ξ, i.e. how energy is stored and dissipated.

One feature of the current model is "stress relaxation" in response to a constant stretch history (observed in Fig. 3) and "creep-like behavior" in response to constant inflation pressures (observed in Fig. 4). Stress decreases as the moduli of the material diminish due to degradation; similarly, the annulus creeps outwards in response to a constant inflation pressure for the same reasons. Nevertheless, these behaviors are markedly different from their viscoelastic counterparts: viscoelastic materials can be viewed as materials whose response changes from an evolving set of natural configurations (Rajagopal and Srinivasa 2004), whereas in the present model, it is the moduli that are decreasing and are responsible for such characteristics. Furthermore, Rajagopal and Wineman (2004) observed comparable behavior in the stress relaxation response of viscoelastic materials that can age and in fact have separated the contribution due to aging and due to the inherent viscoelasticity of the material in the stress relaxation response of a cylinder under torsion.

The response of biodegradable materials as degradation proceeds is dramatically different from common non-degradable biomaterials. Therefore, common design tools and previous expertise in permanent devices cannot be directly applied to biodegradable devices. These differences must be understood and accounted for in the device rationale, starting at the initial state of the design process.

Under constant loads, degradation and depreciation leads to greater deformations, and vice versa ad infinitum. This situation will lead to failure of the device at some point in time. This expected failure must be predicted and the device carefully designed. After the deployment of a biodegradable stent, the elastic recoil of the artery will promote a slight deflation of the stent. This deflation will increase progressively as the biodegradable material loses its ability to withstand load. On the other hand, in the preparation of tissue engineered of arterial conduits, the balance between the inner pressure of the perfusing fluid and the outer pressure of the fluid bath must account for degradation of the material over time. If the process of extracellular matrix production fails to replace the biodegradable scaffold at a sufficient rate (a process not modeled here), the annulus will creep over time due to the depreciation of mechanical properties.

Inhomogeneity of degradation is another important feature of some biodegradable devices that could seriously impact clinical outcomes. Most working conditions involve inhomogeneous deformations, which can cause some parts of the implant to degrade faster than others. Existing designs of cardiovascular stents are characterized by a strain field that is mostly confined to location where struts curve or bend. With a biodegradable material, these locations will suffer greater degradations and failure most likely will occur first at these points. On the other hand, straight portions of the struts will remain mostly non-degraded, and can pose embolic problems. Direct application of bare metal stent designs to fully biodegradable stent technology is ill posed from its inception.

The limitations of this study include the lack of relevant experimental data on the behavior of the polymer as it degrades under mechanical loading. Other relevant factors influencing the degradation process were not considered, such as swelling and diffusion of water inside the body, changes in temperature, and autocatalysis due to degradation byproducts - the analysis was confined to the mechanical aspects of strain-modulated degradation and depreciation of mechanical properties as its sole effect.

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