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Constitutive modeling of biodegradable polymers: Hydrolytic degradation and time-dependent behavior

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ABSTRACT

A large range of biodegradable polymers has been used to produce implantable medical devices. Apart from biological compatibility, these devices shall be also functional compatible and perform adequate mechanical temporary support during the healing process. However, the mechanical behavior of biodegradable materials during its degradation, which is an important aspect of the design of these biodegradable devices, is still an unexplored subject. Based on the literature, the mechanical behavior of biodegradable polymers is strain rate dependent and exhibits hysteresis upon cyclic loading. On the other hand, ductility, toughness and strength of the material decay during hydrolytic degradation. In this work, it is considered a three-dimensional time-dependent model adapted from the one developed by Bergström and Boyce to simulate the performance of biodegradable structures undergoing large deformations incorporating the hydrolysis degradation. Since this model assumes that the mechanical behavior is divided into a time independent network and a non-linear time-dependent network, it enables to simulate the monotonic tests of a biodegradable structure loaded under different strain rates. The hysteresis effects during unloading–reloading cycles at different strain levels can be predicted by the model. A parametric study of the material model parameters evolution during the hydrolytic degradation was conducted to identify which parameters are more sensible to this degradation process. The investigated model could predict very well the experimental results of a blend of polylactic acid and polycaprolactone (PLA–PCL) in the full range of strains until rupture during hydrolytic degradation. From these results and analyses, a method is proposed to simulate the three-dimensional mechanical behavior during hydrolytic degradation.

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1. Introduction

Biodegradable polymers can be obtained from renewable resources or from chemical synthesis. A large range of mechanical properties and degradation rates are possible among these polymers. However, the prediction of the mechanical behavior of the biodegradable devices is fairly complex, because not only the mechanical properties evolve during degradation, but also these devices operate under large strain deformation fields. Due to the nonlinear response of the stress vs. strain relation, the classical linear elastic model is not valid for simulation under large strains. Current designs of biodegradable devices have been carried out by considering elastic or elastoplastic behavior and neglect any changing on the mechanical behavior caused by degradation (Moore et al., 2010). For many biomedical applications, the biodegradable polymeric structures are submitted to cyclic loading above the elastic limit. Hence, they are prone to accumulate plastic strain at each cycle, which may lead to laxity and consequent failure, such as in ligament augmentation devices (Vieira et al., 2009). For instance, Grabow et al. (2007) showed that significant creep of polylactides (PLA) under a constant load leads to strain accumulation and collapse.

Concomitantly to its nonlinear response, the mechanical behavior of polymeric materials is also temperature and rate dependent (Bardenhagen et al., 1997). However, in this work, only the rate dependent influence has been investigated. Temperature dependence may be neglected since isothermal hosting environment is always verified. The blend of polylactic acid and polycaprolactone (PLA–PCL), has been evaluated in previous works by the authors (Vieira et al., 2011a,b, 2013). The nonlinear viscoelastic characteristics of PLA were also verified by Soares (2008) and Grabow et al. (2007). The mechanical behavior of biodegradable polymers, such as PLA–PCL, also exhibits hysteresis, i.e. energy dissipation in form of heat, upon cyclic loading (Vieira et al., 2013). Therefore, time-dependent constitutive models are required to simulate such phenomena.

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A constitutive model for a mechanical analysis is a relationship between the response of a body (for example, strain state) and the stress state due to the forces acting on the body, which can include the environmental effects. The actual models can be divided into two categories: the time-independent models and the time-dependent models (Ferry,1980). Several constitutive models have been proposed for non-degraded polymers and elastomers. Most of the earlier research works (Flory, 1977; James and Guth, 1943; Treloar, 1975; Wall and Flory, 1951) was devoted to the prediction of the time-independent response. Other more successful models are the 8-chain network model developed by Arruda and Boyce (1993a), and more recently the micro-sphere model developed by Miehe et al. (2004).

As observed in polymers, it is known that the stress in a biodegradable polymer will relax towards an equilibrium state after being subjected to a strain-step (Miller and William, 1984). This relaxed state has been simulated by linear elastic, elasto-plastic or hyperelastic models, but disregarding the rate dependency effect. Mechanical properties of biodegradable polymers are commonly assessed within the scope of linearized elasticity, despite the large strains, which are observed before material fracture. Classical models such as the neo-Hookean and Mooney–Rivlin models, usually applied for incompressible hyperelastic materials, have been used to predict mechanical behavior until rupture of non-degraded PLA (Garlotta, 2001; Lunt, 1998) under quasi-static monotonic loading. However, all of them neglect changes in the properties of the material during degradation process.

To consider time dependency, dissipative elements described by time inhomogeneous relations must be used in the model formulation. The simplest viscoelastic models consider a linear combination of springs (using the Hooke's law) and dashpots (using Newtonian damper with linear viscosity). The classical examples of these simple models are the Maxwell and Kelvin–Voigt models, in which spring and dashpots are organized in series or in parallel, respectively. More complex variants of these simple models can be found at the literature (Arruda and Boyce, 1993b; Bardenhagen et al., 1997; Bergström et al., 2002; Boyce et al., 1988; Dafalias, 1991; Drozdov and Gupta, 2003; Fancello et al., 2006; Harren, 1995; Hasan and Boyce, 1995; Hausler and Sayir, 1995; Holzapfel, 1996; Johnson et al., 1995; Lubarda et al., 2003; O'Dowd and Knauss, 1995; Reese and Govindjee, 1998; Rubin, 1987; Zdunek, 1993). These models can simulate the non linear viscoelastic, viscoplastic and hysteretic response of polymers. They are based on the concept of networks, combining elastic, sliding and dissipative elements, in order to simulate the time-dependent response of the material.

From the author's knowledge, only few methods were developed to predict the mechanical behavior during hydrolytic degradation. Those methods are based on hyperelastic models (Soares et al., 2010; Vieira et al., 2011a), or on quasi-linear viscoelastic models (Muliana and Rajagopal, 2012), or on phenomenological viscoplastic models (Khan and El-Sayed, 2012). However the calibration and validation of those methods were restricted to moderate deformations. Albeit, the Bergström–Boyce model (Bergström and Boyce, 1998) is a viscoelastic model, which simulates the performance of polymers undergoing large deformations. Since it is a physical inspired polymer model, it can be calibrated through a relative small set of simple mechanical tests, such as uniaxial loading, to provide accurate predictions for different loading cases (Bergström et al., 2002). These comprise monotonic loading under different strain rates, including hysteresis effect, and unloading–reloading cycles at different strain levels (Bergström et al., 2002).

Considering the latest arguments, a parametric study based on the adapted Bergström–Boyce model is performed in this work for a polymeric blend of PLA–PCL. Thus, the evolution of the material model parameters during hydrolytic degradation is determined, analyzing those parameters more sensible to this degradation process. Therefore, the limitation and potentialities of the adapted Bergström–Boyce model to simulate a biodegradable polymer over large range deformations under hydrolytic biodegradation are evaluated and discussed. Finally, a new method is proposed, based on these analyses, to simulate the three-dimensional time-dependent mechanical behavior during hydrolytic degradation. Although the present approach is applied to a PLA–PCL blend by using experimental data, the authors verified the applicability of the proposed method for other biodegradable polymers, such as polydioxone (PDO) and polyglycolic acid (PGA), which also exhibit time-dependent mechanical behavior. In a previous work (Vieira et al., 2010), it is possible to find experimental results for monotonic tensile tests during degradation. The application of the method proposed in this work will be addressed in the following papers.

2. Hydrolytic degradation

In general, the most important degradation mechanism for biodegradable polymers in biomedical applications is chemical degradation via hydrolysis or enzyme-catalyzed hydrolysis (Göpferich, 1996). It is well known that the mechanical behavior will evolve during time (see Fig. 1a), due to hydrolytic chain scission in the polymeric macromolecules. The reduction of molecular weight is linked to this evolution in mechanical response of biodegradable polymers (see Fig. 1b).

Hydrolysis has been traditionally modeled by using a first order kinetics equation based on the random scission kinetic mechanism of hydrolysis, according to the Michaelis–Menten scheme (Bellenger et al., 1995). 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 split by hydrolysis. The following first-order equation describes the hydrolytic process (Farrar and Gilson, 2002), in terms of the rate of formation of carboxyl end groups:

$$\frac{dc}{dt} = kewc = uc \tag{1}$$

where e, c and w are the concentrations of ester groups, carboxyl groups and water in the polymer, respectively. k is the hydrolysis rate constant and t is the degradation time. u is the hydrolytic degradation rate of the material, that can be determined by measuring strength or molecular weight evolution during hydrolytic degradation (see Vieira et al., 2011a). Since the concentration of carboxyl end groups is given by $c = 1/M_n$, where M_n is the number-average molecular weight of the polymer, the evolution of the , number-average molecular weight is given, after integration, by:

$$M_{n_t} = M_{n_0} e^{-ut} \tag{2}$$

It has been shown by Vieira et al. (2011a) that the fracture strength σ during degradation has a similar evolution to the number-average molecular weight of the polymer (see Fig. 1b), and can be predicted by the following equation:

$$\sigma_t = \sigma_0 e^{-ut} = \sigma_0 e^{-kwet} \tag{3}$$

where σ_t and M_{n_t} are the strength and the number-average molecular weight of the polymer at degradation time t; σ_0 and M_{n_o} are the corresponding initial (non-degraded) values. In Fig. 1a) is shown the mechanical response to uniaxial monotonic tensile tests until rupture, of PLA–PCL fibers during hydrolytic degradation. The evolution of fracture strength, according to Eq. (3), is similar to the evolution of the number-average molecular weight of the polymer (see Fig. 1b) in accordance to Eq. (2). In a semi logarithmic representation of

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