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A constitutive law for degrading bioresorbable polymers

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ABSTRACT

This paper presents a constitutive law that predicts the changes in elastic moduli, Poisson's ratio and ultimate tensile strength of bioresorbable polymers due to biodegradation. During biodegradation, long polymer chains are cleaved by hydrolysis reaction. For semi-crystalline polymers, the chain scissions also lead to crystallisation. Treating each scission as a cavity and each new crystal as a solid inclusion, a degrading semi-crystalline polymer can be modelled as a continuum solid containing randomly distributed cavities and crystal inclusions. The effective elastic properties of a degrading polymer are calculated using existing theories for such solid and the tensile strength of the degrading polymer is predicted using scaling relations that were developed for porous materials. The theoretical model for elastic properties and the scaling law for strength form a complete constitutive relation for the degrading polymers. It is shown that the constitutive law can capture the trend of the experimental data in the literature for a range of biodegradable polymers fairly well.

1. Introduction

There is a worldwide attempt to develop and use bioresorbable medical implants such as coronary stents and fixation screws made of bioresorbable polymers. The bioresorbable screws and plates have been used for internal fixation in patients for a number of years. The bioresorbable stents are currently being used in several countries. Unlike permanent implants made of stainless steels or titanium alloys, bioresorbable implants "disappear" after serving their functions in the human body. When designing bioresorbable implants, it is important to understand how the mechanical properties of the polymer materials change as they degrade. Degradation of bioresorbable polymers occurs by uptake of water and attack of water molecules to ester bonds of the polymer chains in a time dependent process known as hydrolysis degradation (Buchanan et al., 2008). The basic "damage" mechanism is polymer chain scission caused by the hydrolysis reaction. These chain scissions lead to significant reduction in the mechanical property of the polymers (Ashby and Jones, 2005; Tsuji, 2000, 2002, 2003; Tsuji and Del Carpio, 2003; Tsuji and Muramatsu, 2001). Some typical bioresorbable polymers are semi-crystalline. New nano-sized crystals can be formed as the consequence of the extra mobility of the polymer chains due to chain scission. The increase in crystallinity can be as high as 40% (Bouapao et al.,

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Nomenclature

$\Omega^{(\alpha)}$	Inhomogeneities ($\alpha=1,2$)
$C_I^{(\alpha)}$	Elastic stiffness of inhomogeneities
$K_I^{(\alpha)}$	Bulk modulus of inhomogeneities
$\mu_I^{(\alpha)}$	Shear modulus of inhomogeneities
$f_I^{(\alpha)}$	Volume fractions of inhomogeneities
$\overline{\sigma}_I^{(\alpha)}$	Average stress of inhomogeneities
$\overline{\varepsilon}_I^{(\alpha)}$	Average strain of inhomogeneities
f_M	Volume fraction of matrix
C_M	Elastic stiffness of matrix
K_M	Bulk modulus of matrix
μ_M	Shear modulus of matrix
$\overline{\sigma}_M$	Average stress of matrix
$\overline{\varepsilon}_M$	Average strain of matrix
C	Effective elastic stiffness of material
K	Bulk modulus of the material
μ	Shear moduli of material
ν	Poisson’s ratio of material
$\overline{\sigma}$	Average stress of material
σ^0	Uniform applied stress
ε_{kk}^0	Remote hydrostatic pressure
ε_{12}^0	Remote shear strain
r	Radius of cavities
$\overline{M}_n$	Number averaged molecular weight normalised by its initial value
M_{n0}	Initial number average molecular weight (g/mol)
M_{unit}	Molecular weight of the repeating unit of the polymer chain (kg/mol)
C_{e0}	Initial concentration of ester bonds (mol/m^3)
α, β	Empirical parameters for oligomer production (dimensionless)
ρ	Density (g/m^3) of degrading polymer
ρ_0	Initial Polymer density (g/m^3) (before degradation)
m	Degree of polymerisation of the oligomers (dimensionless)
R_s	Total number of chain-scissions per unit volume (mol/m^3)
$\overline{R}_s$	Total number of chain-scission normalised by initial number of ester bond per unit volume
X_{c0}	Initial degree of crystallinity
X_c	Scission-induced crystallinity
ω	Number of ester units of crystalline phase per unit volume
N_{chain0}	Initial number of molecular chains per unit volume including crystalline phase
E_0	Initial Young's modulus
$E_I^{(2)}$	Young modulus of the crystals to fit the data
P^*	A property of the metal foam
P_s	A property of the matrix of metal foam
ρ_s	Density of the matrix of metal foam
$f_I^{(1)}$	Density of cavities (porosity)
α	A constant
σ_t	Tensile strength of the porous metal foam
σ_{t0}	Initial tensile strength
$\sigma_{c,s}$	Initial compressive strength of the matrix of metal foam

2009; Saha and Tsuji; 2006, Tsuji et al., 2004). Because the crystals have a higher Young’s modulus than the amorphous phase, the new crystals act as an enhancement phase that increases Young’s modulus of the semi-crystalline polymer. Despite a polymer chain cleavage is an event at the atomistic scale, each chain-scission can be treated as an effective spherical cavity in the polymer. A new crystal on the other hand can be treated as an inclusion of different Young’s modulus. It is then possible to calculate the effective moduli of a degrading polymer for continuum solid containing these cavities and inclusions. A representative volume element (RVE) for the polymer is considered and it is assumed that the size of the cavities and crystals remains constant, but their numbers increase as degradation proceeds. Gleadall (2014) performed such calculations using finite element analysis. However the numerical calculations could only provide empirical fitting equations for Young’s modulus. These fitting functions are unnecessarily dependent on the details of the finite element models. Furthermore Gleadall did not consider the full constitutive response and ignored Poisson ratio and strength of degrading polymers which are important if one wishes to use the constitutive law for device design. This paper presents a complete and analytical constitutive law for degrading polymers.

Numerous studies have been carried out for the effective moduli of composite materials. The Voigt approximation is probably the simplest model which assumes the strain throughout a composite is uniform and equal to the average strain. The Reuss approximation assumes that the stress throughout a composite is uniform and equal to the average stress. Hill proved that the Voigt approximation and Reuss approximation are actually the upper and lower bounds of the effective elastic moduli (Hill, 1963). Hashin and Shtrikman (1962) also provided bounds for the elastic moduli and tensors of isotropic composites reinforced by aligned continuous fibres or randomly positioned particles which are similar to Walpole bounds but better than the Voigt and Reuss bounds (Walpole, 1966). The effective moduli estimated by Eshelby using the EIM method is only valid in the limit of low porosity (dilute limit) (Eshelby, 1957). The EIM yields the same result as the dilute approximation which ignores the interaction between reinforcing particles. The self-consistent schemes (SCS) use material properties of a composite for infinite medium, i.e. the inclusion phase is assumed to see an effective medium of unknown properties. Hill presented the overall constraint tensor for an isotropic continuum containing a spherical cavity based on the self-consistent method. He assumed that inclusions are spheres distributed in a way such that the composite is statistically isotropic overall (Hill, 1963). Mackenzie (1950) was probably the first who calculated the elastic constants of solid containing circular cavities. His scheme, known as the generalised self-consistent scheme (GSCS), assumes that