



## Review

## Lifetime prediction of biodegradable polymers



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## ABSTRACT

The determination of the safe working life of polymer materials is important for their successful use in engineering, medicine and consumer-goods applications. An understanding of the physical and chemical changes to the structure of widely-used polymers such as the polyolefins, when exposed to aggressive environments, has provided a framework for controlling their ultimate service lifetime by either stabilising the polymer or chemically accelerating the degradation reactions. The recent focus on biodegradable polymers as replacements for more bio-inert materials such as the polyolefins in areas as diverse as packaging and as scaffolds for tissue engineering has highlighted the need for a review of the approaches to being able to predict the lifetime of these materials. In many studies the focus has not been on the embrittlement and fracture of the material (as it would be for a polyolefin) but rather the products of degradation, their toxicity and ultimate fate when in the environment, which may be the human body. These differences are primarily due to time-scale. Different approaches to the problem have arisen in biomedicine, such as the kinetic control of drug delivery by the bio-erosion of polymers, but the similarities in mechanism provide real prospects for the prediction of the safe service lifetime of a biodegradable polymer as a structural material. Common mechanistic themes that emerge include the diffusion-controlled process of water sorption and conditions for surface *versus* bulk degradation, the role of hydrolysis *versus* oxidative degradation in controlling the rate of polymer chain scission and strength loss and the specificity of enzyme-mediated reactions.

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## Nomenclature

|                 |  |
|-----------------|--|
| $\alpha$        | Diffusion porosity constant  |
| $\beta$         | A constant introduced to regulate the contribution of autocatalysis                              |
| $\gamma$        | Axial stretch ( $\gamma = 1 + \epsilon$ ) (where $\epsilon$ is the nominal strain)               |
| $\delta^2$      | Cohesive energy density of the polymer   |
| $\delta_1^2$    | Dispersion forces  |
| $\delta_2^2$    | Polar forces   |
| $\delta_3^2$    | Hydrogen bonding forces  |
| $\epsilon$      | Nominal strain   |
| $\epsilon_t$    | Erosion number   |
| $\vartheta$     | Fraction of the substrate surface occupied by the ES complex                                     |
| $\theta$        | A rate constant that accounts for the differences in the reactivity of polymer functional groups |
| $\Lambda$       | Thiele modulus   |
| $\lambda$       | Hydrolysis rate constant specific to a polymer   |
| $\lambda'$      | Pseudo first order rate constant   |
| $\lambda''$     | Revised rate constant  |
| $\lambda_{E_i}$ | Rate constant for hydrolysis of each corresponding type of ester bond ( $E_i$ )                  |
| $\mu_{g_p}$     | Polymer weight loss in $\mu\text{g}$   |
| $\mu_{g_z}$     | Mass of enzyme present in $\mu\text{g}$  |
| $v_0$           | Rate of a reaction   |
| $\rho$          | Polymer density  |
| $\rho_W^\infty$ | Water density  |
| $\sigma$        | Polymer strength   |

|                 |  |
|-----------------|--|
| $\sigma_0$      | Nominal stress   |
| $\sigma_x$      | Tensile stress ( $\text{N m}^{-2}$ )   |
| $\sigma_\infty$ | Polymer strength at a theoretical infinite $\bar{M}_n$   |
| $\varphi_A$     | Concentration of ester bonds in the amorphous fraction (mol/L)   |
| $\omega$        | Inverse molar volume of the crystalline phase  |
| $\phi$          | Activation volume coefficient ( $\text{m}^3 \text{mol}^{-1}$ )   |
| $A$             | Pre- exponential factor for the hydrolysis reaction rate coefficient   |
| <i>Area</i>     | Substrate surface area   |
| <i>BSR</i>      | Tensile breaking strength retention (given by $BSR = \frac{\sigma_0 - \sigma}{\sigma_0} = 1 - \frac{\sigma}{\sigma_0}$ ) |
| $c_1$           | A constant of integration that accounts for the hydrolysis rate and crystallinity  |
| $c_2$           | Ratio of the initial concentrations of acids and ester bonds; $c_2 = [\text{COOH}]_0 / [E]_0$                            |
| $C_\infty$      | The amount of starch degraded at the end point of the enzymatic hydrolysis reaction                                      |
| $c_m$           | Molar concentration of hydrolysed monomers   |
| $c_{ol}$        | Molar concentration of ester bonds in the oligomers (mol/L)  |
| $C_m^b$         | Diffusion of monomers accounting for dissociation of acid end group  |
| $C_t$           | The starch degraded (expressed as mass per unit volume) at incubation time $t$   |
| $D$             | Diffusion coefficient  |
| $D_0$           | Intrinsic diffusion coefficient  |
| $D_\infty$      | Diffusivity of water into an intact, dry polymer   |

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